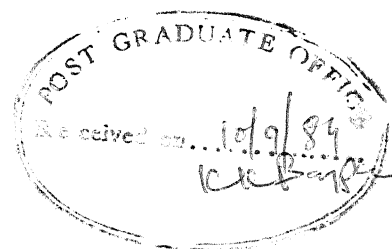# MANGANESE SULPHUR INTERACTIONS IN IRON CARBON ALLOYS

A Thesis Submitted
In Partial Fulfilment of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

by
ASOK KUMAR PATTJOSHI

to the

DEPARTMENT OF METALLURGICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR
SEPTEMBER, 1984

CERTIFICATE

Certified that the work reported in this thesis entitled 'Manganese Sulphur Interactions in Iron-Carbon Alloys' by A.K. Pattjoshi has been carried out under my supervision and has not been submitted elsewhere for the award of degree.

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To my wife goes special thanks for having hoed this long row with me. Her encouragement was often sought and much needed.

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A.K. PATTJOSHI

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MANGANESE-SULPHUR INTERACTIONS IN IRON CARBON ALLOYS

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Studies on sulphur control in iron making and steel making processes or by means of external treatment of metal in the ladle have gained importance in recent years to meet challanges for production of low sulphur steel at lower cost for newer and newer applications in space, ocean, defence etc. Basic studies are important in understanding the mechanism of sulphur removal from the metal to slag. Thermodynamics of sulphur reactions and desulphurising powers of various blast furnace and steel making slags have been investigated by many workers by equilibriating the melt with known H_2/H_2S ratio or with a known quantity and composition of slag at a fixed temperature. In the present work attempts are made to study the effect of Mn on the desulphurisation of iron-carbon melts due to formation of MnS with and without addition of some oxide slags of $CaO-SiO_2-Al_2O_3$ system in the temperature range of $1200^\circ-1400^\circ C$. Such temperatures usually occur in the transit of

the hot metal from the blast furnace to the steel making unit and in presence of Mn, sulphur drops are expected to occur.

Laboratory experiments included fabricating a silicon carbide furnace, making iron-carbon alloys, melting the alloy under argon atmosphere in a graphite crucible, drawing the samples carefully with a quartz tube and the analysis of sulphur and manganese in the laboratory.

The effect of Mn in metal on the desulphurising power of oxide slags was studied by making synthetic slags of $CaO-SiO_2-Al_2O_3$ in the laboratory and equilibrating the melt at $1400^\circ C$ with those slags for 4-6 hours of duration. Samples were either drawn from the melt or taken from the solidified mass in the crucible after the duration of experiment. Pure lime was also used as a desulphuriser in some experiments for comparison purposes. Reliability of data was checked by repeating a few experiment, by making more than one analysis of some samples and by calibrating the apparatus with a standard steel sample supplied by British chemical standards. Thermocouples were suitably calibrated against standard thermocouples and with melting point of pure copper. Raw materials were characterised by X-ray diffraction and by chemical analysis in the laboratory.

Experiments were done by stepwise addition of manganese to the melt of Fe-C-S at constant temperature or by cooling and heating of Fe-C-Mn-S melt. The solubility

of sulphur determined experimentally at lower temperatures
of $1200^\circ C$ matched well with the reported data of Morris*,
where as at $1400^\circ C$ the sulphur levels in the melt were found
to be less in the present investigation.

A regular solution model has been proposed for
finding the activity coefficient of sulphur at temperatures
lower than $1600^\circ C$ as data existed in the literature only at
$1600^\circ C$.

The calculated values of the sulphur content in carbon
saturated metal at different temperatures and manganese
contents of metal were compared with the experimental results.
Good agreement was reached in most of the cases if the activities
of MnS and FeS in slag were taken to be the same as their weight
fractions and a discrepancy of -1.0 to -1.8 kcal/mole in the
reported standard free energy of formation of MnS was allowed.
These limits are within the accuracy of the reported data.

From the slag metal equilibrium studies at $1400^\circ C$,
manganese upto 2 pct. was found to decrease the sulphur
content of metal at all combinations of slag volume (10 to
20 pct.) and slag basicity (CaO/SiO_2 ratio of 1 to 2). A
multicomponent multiphase mathematical model was developed to
analyse the experimental findings. Sulphur partition ratios
were calculated both from the model and the experimental data.
Exact role of manganese in lowering the sulphur content of
the iron-carbon alloy melt could not be identified . More

* J.P. Morris, J. df Metals, (September 1952), p. 939-940.

scientific data under the laboratory and plant condition are recommended to understand the mechanism of sulphur transfer from slag to metal in presence of manganese in the melt.

CHAPTER - I

INTRODUCTION

1.1 Effect of Sulphur on Mechanical Properties of Steel

Sulphur in steel is considered to be harmful, because the presence of sulphur lowers the mechanical properties of steel. Free cutting steel is the only grade of steel where the sulphur content is kept deliberately high, i.e. 0.22 weight pct or more. Low sulphur in steel is essential for improved notch toughness, ductility, cold pressing properties and to avoid cracking failure as well as directional anisotropy in mechanical properties on hot working. For the production of quality steel and for super duty applications, the sulphur in steel should be generally less than 0.01 percent. It is generally specified that the final product i.e. steel should have 0.025-0.040 percent sulphur for general applications and the modern trend is towards lower and lower sulphur contents in steel.

Some of the detrimental effects of sulphur in steel are elaborated further below.

1.1.1 Ductility of steel

A major factor determining the yield in hot working operations is the ductility of steel. Some steels having lower ductility restrict their range of working temperature. Elements which form low melting point compounds or inclusions

deform differentially leading to cracking or large scale fracture. Sulphur in steel is known to form a low melting point compound FeS and contributes to red shortness. This red shortness is manifested as a marked lack of ductility in the temperature range $850-1050^\circ C$ when sulphur content is greater than 0.005 percent. The addition of manganese above a critical value, improves the ductility of the steels which are susceptible to red shortness. The stoichometric ratio of 'Mn' to 'S' in MnS is 1.72 and at ratio lower than this ,some 'S' should be present in inclusions as FeS or (Fe, Mn)S. The loss of ductility increases with increasing amount of inclusion material.

1.1.2 Anisotropy

The sulfides are very plastic at high temperatures and they get elongated in the direction of rolling. They thus contribute to the anisotropy of mechanical properties relative to the longitudinal and transverse directions. Sulfides lower the ductile fracture level of the steel longitudinally as well as transversely.

1.1.3 Impact

In the case of nickel maraging steels, the influence of sulphur on impact properties is highly pronounced and maximum of 0.005 to 0.01 pct, of sulphur can be allowed in such steels. In high strength steels even lower sulphur contents have a marked influence on resistance to sudden crack propagation in the longitudinal as well as in the transverse direction.

1.1.4 Fatigue

Depending upon the steel composition sulphur lowers its transverse fatigue resistance. An increase in sulphur content of steel has detrimental effect on transverse fatigue resistance.

1.1.5 Weld defects

Lamellar tearing is considered to be the most serious cracking problem during welding of structural and pressure vessel steels. Sulphur in steel gives rise to lamellar tearing in weld joints. Also sulphur imparts porosity in weld joints. The concentration, size and distribution of sulphide inclusions are controlling factor for the problems in weld joints.

1.1.6 Conclusion

It is clear from the foregoing sections that presence of sulphur in steel is not at all desirable. The sulphur levels in structural steels should be less than 0.035 Pct and less than 0.02 Pct for quality steels.

To achieve low sulphur in steel, varieties of processes are in operation throughout the world. The origin and control of sulphur in steel are dealt in the following sections.

1.2 Origin of Sulphur in Steel

Bulk of the steel is commercially produced through the traditional route of blast furnace/LD or blast furnace/ openhearth, while a small fraction is also produced by other methods such as electric arc furnace melting of scrap, DR/EAF route etc.

The major source of sulphur input to the blast furnace is through coke, with a very small fraction entering with sinter or iron ore. Sulphur in the blast furnace is favourably distributed between slag and metal due to the reducing conditions inherent in blast furnace smelting of pig iron. A typical sulphur balance in a blast furnace is shown in Table 1.1.

It is apparent that a very small fraction of sulphur entering with the burden leaves with flue gases. As coke burns at the tuyeres, sulphur is picked up by H_2 and CO gases to form H_2S and COS. As these gases come in contact with iron bearing and CaO bearing materials, sulphur is absorbed to form FeS and CaS and it descends to the bottom along with the rest of materials in the molten form.

1.3 Control of Sulphur in Steel

1.3.1 Sulphur control in blast furnace iron

Sulphur in the charge materials is absorbed by the metal and slag in the bosh or shaft and the final transfer of sulphur from metal to slag occurs in the hearth.

If 'α' the distribution coefficient of sulphur is defined as ratio of wt pct 'S' in slag to wt pct 'S' in metal i.e.

$$\alpha = \frac{(Pct.S)_{slag}}{[Pct.S]_{metal}} \tag{1.1}$$

'S' level in hot metal can be written as follows:

$$[S] = \frac{100\ S_{input}}{1000 + \alpha\ W_{slag}} \tag{1.2}$$

where S_{input} and W_{slag} are the weights of sulphur entering with burden, and slag respectively in kg/THM. It is assumed

Table 1.1 (Ref.1)

A Typical Blast Furnace Sulphur Balance

Material	Sulphur input		Sulphur output	
	Kg/THM	Pct. of Total	Kg/THM	Pct. of Total
Coke	6.0	80	—	—
Charge Materials	1.5	20	—	—
Iron	—	—	0.30	4.0
Flue dust and gases	—	—	0.37	5.0
Slag	—	—	6.83	91.0
Total	7.5		7.5	

that no sulphur leaves with flue gases. Equation (1.2) is plotted in Figure 1.1. Low sulphur in hot metal can be achieved only at higher 'α' values unless slag volumes are excessively high. High slag rates can lead to high coke rates which in turn will increase S_{input} values and hence [S]. Hence the only effective method of producing low [S] iron is to adjust slag composition and temperature in such a manner as to get high sulphur distribution ratios in the blast furnace.

High sulphur distribution ratios are obtained in a blast furnace by maintaining high slag basicity i.e. (CaO+MgO)/SiO$_2$ ratio and high metal temperature and their effects will be discussed later. These factors lead to an increase in carbon rate of the furnace as shown by Flint[2] by the regression analysis of large plant data. He reported that carbon rate increases in a curvilinear fashion as shown in Figure 1.2 and this data is still used by many operators in making the techno economic studies to control sulphur in the blast furnaces.

1.3.2 Sulphur control in steel making

Removal of sulphur from the hot metal during refining by the oxidation process is very limited due to high FeO content of the slag. It is not possible to have sulphur distribution coefficient values greater than 5 or 10 and it puts the limit to which sulphur can be removed in a steel making process. In most of cases only fifty percent of sulphur can be removed from the melt during refining. Favourable conditions for sulphur removal include high basicity i.e.(CaO+MgO/SiO$_2$ ratio,
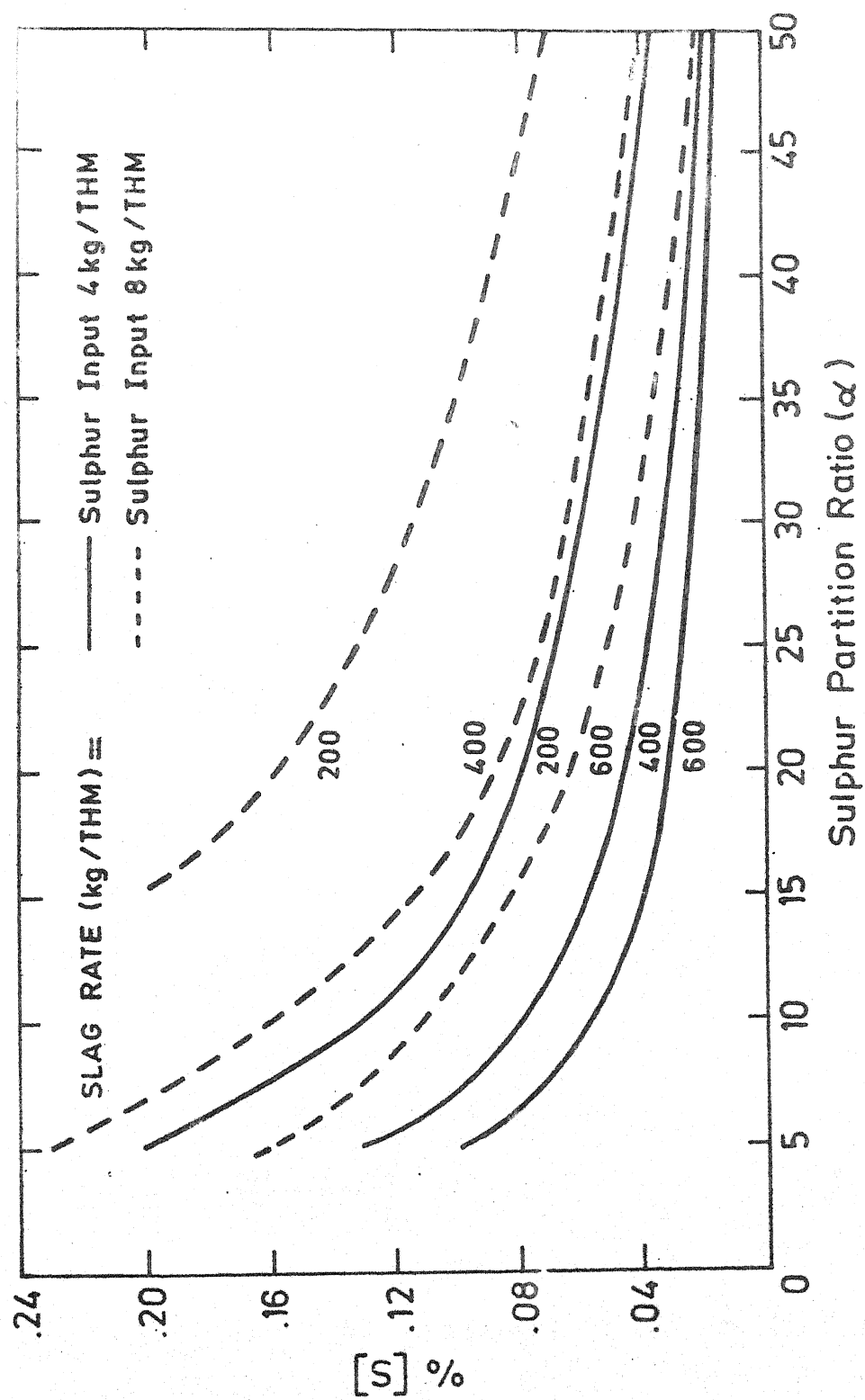
FIG. 1.1 SULPHUR LEVELS IN HOT METAL VERSUS SULPHUR PARTITION RATIO IN BLAST FURNACE.
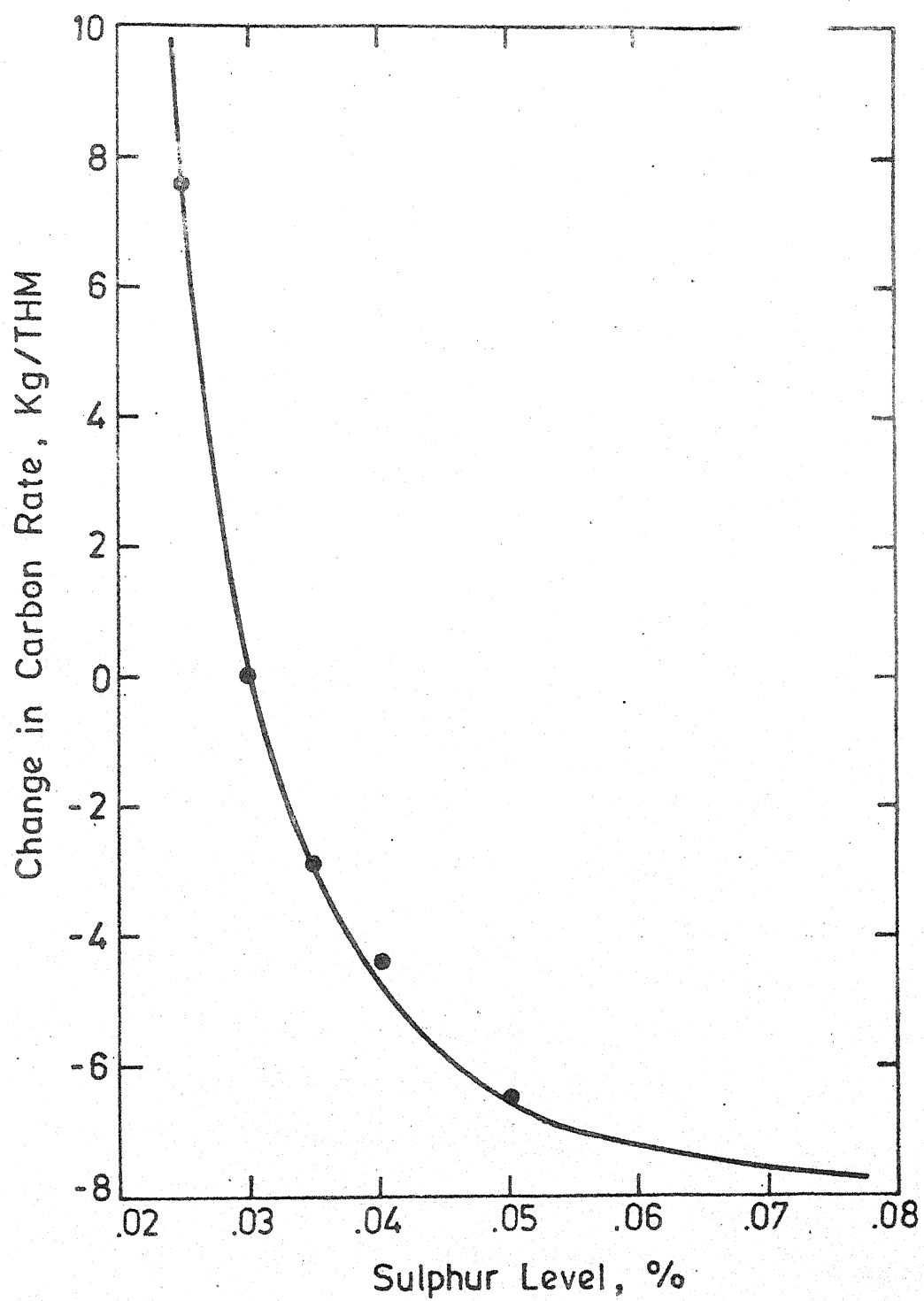
FIG. 1.2 EFFECT OF SULPHUR LEVEL IN HOT METAL ON
CARBON RATE IN BLAST FURNACE. (Ref. 2)

good fluidity of slag and high temperature. Sulphur input via
hot metal, ores, fluxes and fuels must be minimised to produce
low sulphur steel for achieving better mechanical properties.
Typical sulphur balances in open hearth and L.D. processes of
steel making are given in Table 1.2.

Electric furnaces offer ideal conditions for producing
very low sulphur levels because high sulphur distribution ratios
are possible in the reducing period, where FeO in the slag may
not exceed 0.1 percent. Full discussions on the thermodynamics
and kinetics aspects of sulphur reactions during steel making
lie outside the scope of present investigation and are not
reported in this work.

1.3.3 External desulphurisation of iron

External treatment of hot metal to get rid of sulphur
is being widely practised all over the world. The techno-
economic considerations do not normally justify the sulphur
removal to low levels in either blast furnace iron making or
in LD steel making. Desulphurising agents such as soda ash,
lime, calcium carbide or magnesium are either added or injected
to the metal in a suitable manner to enhance the rate of
sulphur removal from the metal to the slag. The slag formed
must be removed from the ladle more effectively otherwise
sulphur reversion may occur during steel making. The following
factors will govern the choice of the process technology and
the desulphurising agents in any steel plant.

(1)   Hot metal composition and its temperature.

(2)   Initial and the final sulphur levels in hot metal.

Table 1.2

A Typical 'S' Balance in LD/BOH Steel Making

Process	Input, Kg/THM		Output, Kg/THM	
	S_{in}		S_{out}	
LD	Hot metal	0.48	Steel	0.35
	Scrap	0.07	Slag	0.20
	Total	0.55	Total	0.55
BOH	Hot metal	0.13	Steel	0.250
	Scrap	0.15	Slag	0.135
	Lime stone and dolomite	0.06		
	Fluorspar	0.020		
	Flame gasses	0.025		
	Total	0.385	Total	0.385

(3)   Space limitations in the plant.

(4)   Cost of installation of desulphurisation unit and operation costs.

(5)   Effectiveness of slag removal after desulphurisation.

(6)   Availability and cost of desulphurising agents.

The following difficulties may be encountered during any external desulphurisation:

(1)   Freezing of the top layer of metal in the ladle may occur to give high skull losses. This also makes addition of desulphurising agents to the bath very difficult.

(2)   Sulphur rich blast furnace slags may accompany the metal and create difficult conditions for 'S' removal.

(3)   Ladle lining may get damaged due to addition of some desulphurising agents.

(4)   Environmental problems.

(5)   Extra handling and delay in the transport of the iron ladles.

(6)   Inefficient removal of slag from the ladles after the external desulphurisation of hot metal.

Various methods and desulphurising agents have been used in the last two decades and those are summarized in Table 1.3.

The station for ladle treatment of metal can be located either near the blast furnace or near the mixer in the steel making shop depending upon the existing conditions in a

Table 1.3

Methods of Desulphurisation

Desulphu-rising agents	Mode of addition	Reagent Quantity Kg/THM	'S'-Range Pct.	Temperature drop ^{o}C	Remarks
Soda ash	Bulk addition	10	.10-.035	60-70	Attacks ladle lining,forms corrosive liquid slag
Lime	Injection	10-20	.05-.02	70-100	Large slag volume
Lime - Soda ash	Injection	8-10	.05-.02	50-80	
Calcium Carbide	Injection	4	.05-.02	15-20	Expensive, good for low sulphur
Mg-Coke (45 percent Mg)	Plunging	0.7	.048-.022	5-15	
Mg-granu-les	Plunging	.7-1.2	.05-.005	5-10	Good for very low sulphur

particular plant. It may also be possible to desulphurise
the metal externally in the blast furnace cast house itself
where slag can be removed efficiently in the runner but initial
sulphur will not be known and the process may create practical
troubles for the tapping crew. In most cases a separate external
desulphurisation station is installed between the blast furnace
and mixer for taking all necessary steps and precautions for
the process optimisation.

1.4 Scope of Present Investigation

The present investigation was undertaken primarily to
study the manganese/sulphur interactions in iron carbon
alloys in the temperature range of $1200^\circ - 1400^\circ C$. The role
of manganese on the desulphurising power of oxide slags at
$1400^\circ C$ was also studied as this information was found to be
lacking in the literature. Suitable arrangements were made
to design and conduct a few experiments under controlled
conditions. The experimental results are supplemented by
theoretical calculations based on the available thermodynamic
data relevant to the systems of interest in the present study.

The comprehensive literature review is given in the
next chapter which is followed by full details on the plans
of the present work. Results of the theoretical calculations are
given in Chapter 4 while Chapters 5 and 6 give experimental
details and results respectively. Discussion on the findings
of the present work and comparison with the results of other
investigators are given in Chapter 7. Chapter 8 gives the summary

and conclusions of this work while recommendation for further
work are given in Chapter 9. A complete bibliography is given
at the end of this thesis.

CHAPTER - II

LITERATURE REVIEW

2.1 Introduction

Scientific investigations on desulphurisation of pig

iron started as early as the 1930's and since then much

work has been done to study the slag-metal and gas-metal

equilibria. Some fundamental work pertinent to desulphuri-

sation of iron has also been carried out. A comprehensive

literature survey is presented in this chapter.

2.2 Preliminary Studies

First studies on the desulphurisation of pig iron

were done by Wentrup[3], Holbrook and Joseph[4,5] and Oelsen[6].

Wentrup found that desulphurisation was improved

by lowering the temperature in presence of manganese in

pig iron. For the Fe-S-Ca-O-Mn-Si system, Wentrup defined

the desulphurisation ratio i.e. the distribution of sulphur

between metal and slag by the ratio of Total(S) in slag to[S]

in metal. The values of $\dfrac{\text{Total(S) in slag}}{[\text{S}]_{\text{metal}}}$ was experimentally

found to be 876.5 for slag containing 0.1 pct FeO, 30 pct CaO

and zero pct SiO_2 and 145.2 for slag containing 2.4 wt pct FeO.

Wentrup concluded that if FeO and SiO_2 content of slag were

kept low, then lime in slag could be an effective desulphuriser.

Holbrook and Joseph[4] studied the desulphurising

power of blast furnace slags, and defined it as the ratio

$\dfrac{(S)_{slag}}{[S]_{metal}}$. Their experiments were carried out under
standardized laboratory conditions and revealed that, in
magnesia free slags the desulphurising power increased
rapidly as lime replaced alumina and slowly as alumina
replaced silica. The desulphurising power decreased slightly
with the addition of magnesia to the acidic slags and increased
markedly when magnesia was added to very basic slags.

Systematic work on the distribution of sulphur between
slag and metal by first finding the activity of sulphur in
the iron base alloys was carried out by Chipman and Co-workers[7].
Their findings are described in the following section.

2.3 Activity of Sulphur in Liquid Iron Alloys

2.3.1 Experimental approach to the determination of thermodynamic data

The experimental approach to determine the activity of
sulphur in the melt required the attainment of equilibrium
between the sulphur in the melt and gaseous atmospheres
containing hydrogen and hydrogen sulphide. The reaction and
its equilibrium constant are written as follows:

$$\underline{S} + H_2(gas) = H_2S \ (gas) \qquad (2.1)$$

The standard free energy change of reaction (2.1) can be
written as

$$\Delta G^o_{2.1} = - RT \ln K_{2.1} \qquad (2.2)$$

$$K_{2.1} = \frac{p_{H_2S}}{p_{H_2} \cdot a_S} \qquad (2.3)$$

$$\text{or } K_{2.1} = \frac{p_{H2S}}{p_{H2}} \times \frac{1}{f_S[wt\% \ S]} \qquad (2.4)$$

Where, p_{H_2S} and p_{H_2} are the partial pressures of H_2S and H_2 respectively in the gas mixture, f_s is the activity coefficient of sulphur in the liquid metal and [wt % S] is the percentage of sulphur in the melt.

The activity of sulphur, a_s, in the melt can be described by the following equation;

$$a_s = f_s \ [\text{wt } \% \ S] \tag{2.5}$$

In a multi component system containing solutes 1,2,3,4... $\log f_s$ may be represented by the following equation;

$$\log f_s = \log f_{s_1} + \log f_{s_2} + \ldots \tag{2.6}$$

where, $\log f_{si} = e_s^i \ [\text{wt } \% \ i] \tag{2.7}$

e_s^i is the interaction parameter (Henrian) i.e. the interaction of sulphur with solute 'i' and is defined as $e_s^i = \dfrac{\partial \log f_{si}}{\partial \ [\text{wt}\% \ i]}$ where, $f_s \to 1$ as all the wt of solutes 1,2,3 --- $\to$ 0. Hence at zero concentration of sulphur, the equation (2.4) reduces to the following;

$$K_{2.1} = \frac{p_{H_2S}}{p_{H_2}} \ x \ \frac{1}{[\text{wt } \% \ S]} \tag{2.8}$$

The R.H.S. term of equation (2.8) may be described as $K'_{2.1}$ at any other concentration of sulphur. By fixing p_{H2S}/p_{H_2} ratios and finding the corresponding equilibrium [wt% S] in the melt, $K'_{2.1}$ values can be computed. A typical plot of $\log K'_{2.1}$ versus sulphur percent is shown in Fig. 2.1. By extrapolating $K'_{2.1}$ to zero pct sulphur, value of $K_{2.1}$ can be determined. Then for any finite concentration, activity coefficient of sulphur can be determined as follows;
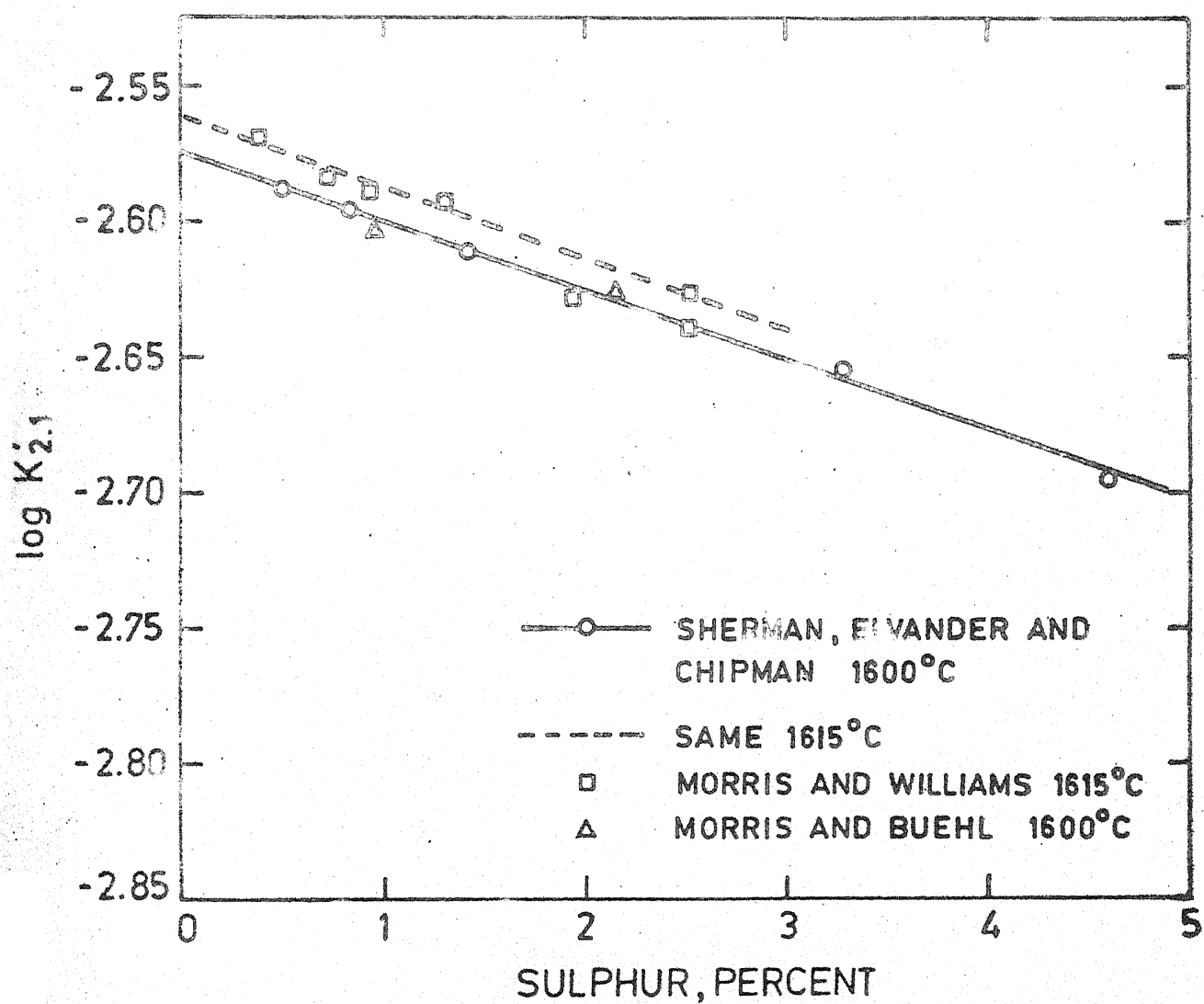
FIG. 2.1 EFFECT OF SULPHUR CONCENTRATION ON $K'_{2.1}$ (Ref. 8, 9, 1

$$f_s = \frac{K'_{2.1}}{K_{2.1}} \qquad (2.9)$$

Similarly activity co-efficient f_{si} in presence of solute 'i' in the melt can be determined and from equation (2.7) corresponding interaction parameter can be calculated.

2.3.2 Fe-S system

The standard free energy of formation of H_2S from gases such as H_2 and S_2 was reported as follows[11];

$$H_2 + \frac{1}{2} S_2 = H_2S \; , \Delta G^o_{2.10} = -21820 + 11.92 \; T \; Cal. \qquad (2.10)$$
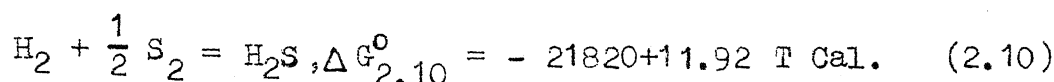
Ban-ya and Chipman[12] calculated the standard free energy of formation of reaction (2.10) by finding the heats and entropies of formation and reported the following;

$$\Delta G^o_{2.10} = -21,530 + 11.73 \; T \; Cal. \qquad (2.11)$$

They also determined the equilibrium constant experimentally as function of temperature in the range of 1500-1600°C and reported the results as follows;

$$H_2 + \underline{S} = H_2S \qquad (2.12)$$

$$Log \; K_{2.12} = -\frac{2350}{T} - 1.34 \qquad (2.13)$$

$$or \quad \Delta G^o_{2.12} = 10750 + 6.13 \; T \; Cal. \qquad (2.14)$$

Combining equations (2.11) and (2.14);

$$\frac{1}{2} S_2 = \underline{S} \; , \Delta G^o_{2.15} = -32,280 + 5.60 \; T \; Cal. \qquad (2.15)$$

Heat of solution of 'S' in iron was estimated as -32.28 Kcal/mole with uncertainty of $\pm$ 2.5 Kcal/mole at 1600°C, but corresponding

uncertainty in ΔG^{o} did not exceed 0.4 kcal.

Activity coefficient 'f_s' varied with 'S' content of iron at 1600°C upto 3 pct 'S' as follows[12];

$$\log f_s = - 0.0282 [\% \text{ S }] \qquad (2.16)$$

From this e_s^s is calculated, -0.0282 which agrees with the value used by investigators earlier[7].

2.3.3 Fe-C-S system

The solubility of sulphur in iron-carbon alloys was investigated by Morris and Buehl[10] by equilibrating the melt with $H_2 - H_2S$ gas mixtures as explained earlier. The results of Morris and Buehl[10] are given in Fig. 2.2.

Increase in the activity coefficient of sulphur due to presence of carbon in the carbon saturated melts was found to be much greater than the earlier studies reported by Kitchner et al[13], whose dafa could not be relied upon due to their wide scatter.

From Fig. 2.2 , e_s^c value could be 0.12 upto carbon concentrations of 1 or 2 wt pct, but for carbon concentration beyond 2 pct, $\log f_s$ versus [wt % C] plot is not linear and equation 2.7 can not be applied directly to find e_s^c value. The slope of $\log f_s$ versus [% C] plot at 4-5 pct carbon level is around 0.24 which has been reported as the interaction parameter value by some investigators later[31].

Some investigators[33] have reported an average value of e_s^c as 0.15 for thermodynamic calculation purposes to give the same value of f_s as determined experimentally by Morris and Buehl[10]
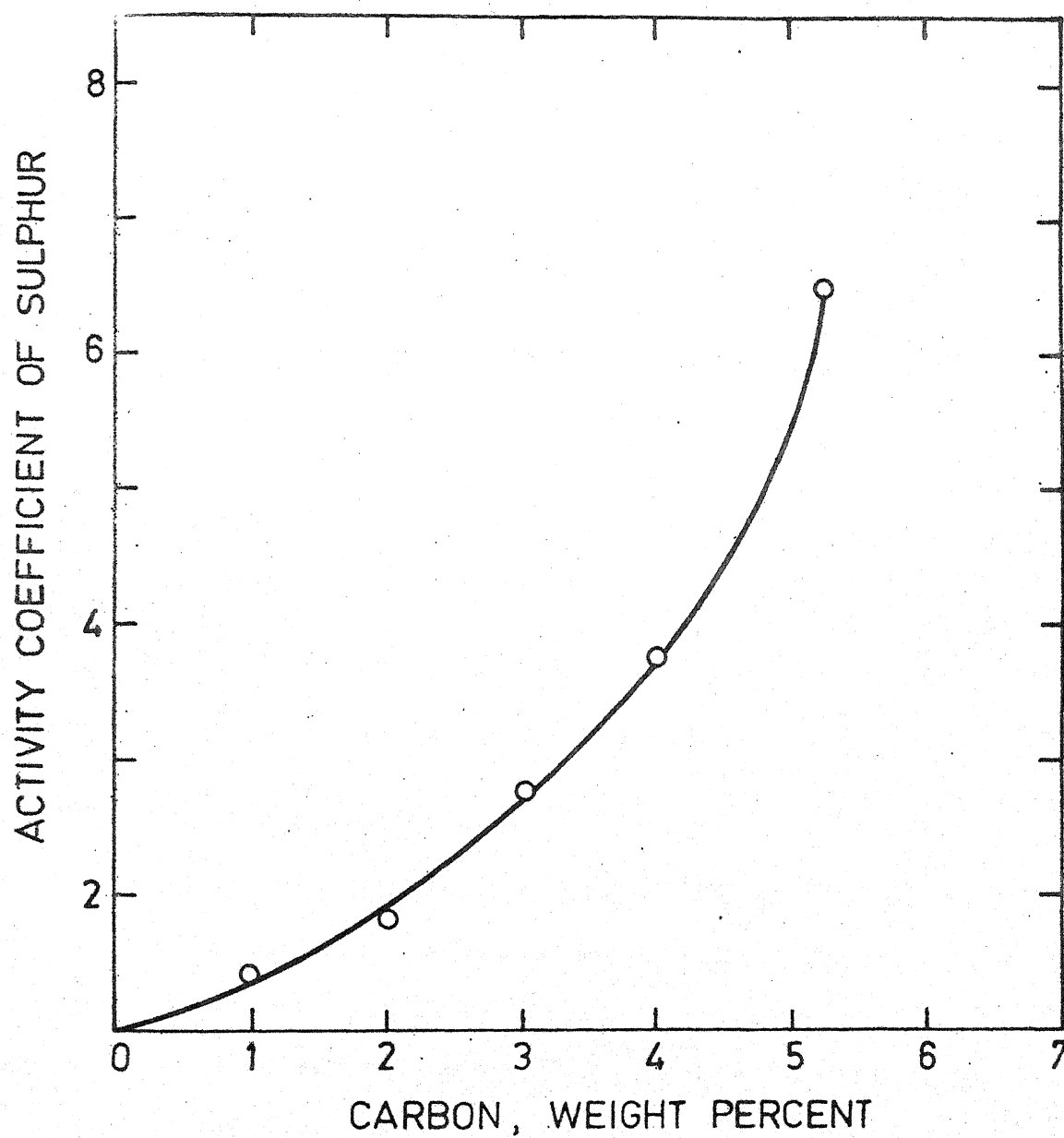
FIG. 2.2 EFFECT OF CARBON CONTENT ON ACTIVITY CO-
EFFICIENT OF SULPHUR IN IRON AT 1600°C. (Ref. 10)

in the carbon level of 3-5 Pct. It might be desirable to use 4.35 pct. Carbon in iron as its standard state as mentioned by Morris and Buehl, who reported the following;

$$\frac{1}{2} S_2(g) = \underline{S} \ (4.35\% \ C) \tag{2.17}$$

$$\Delta G^O_{2.17} = -23,880 + 3.90 \ T \ Cal. \tag{2.18}$$

Equation (2.17) is related to the equation (2.15) by the following;

$$\Delta G^O_{(4.35\% \ C)} = \Delta G^O + RT \ ln \ f^C_s \tag{2.19}$$

f^C_s is found to be 4.2 at 1600^OC at 4.35% C. Since the slope of log f_s versus $[\% \ C]$ plot is 0.24 at this carbon level, f^C_s at any other level of carbon can be determined as follows;

$$Log \ f^C_s = log \ 4.2 + 0.24 \ (x - 4.35) \tag{2.20}$$

where, x is the Wt. Pct Carbon in the melt.

2.3.4 Effect of alloying elements

Sherman and Chipman[7] investigated activity of S in melt of iron containing various alloys such as Mn, P, Al, Cu, Si etc. at 1600^OC. Their results are summarized in Figure 2.3. From log f^i_s versus Wt % i plots in each case, e^i_s can be calculated applying equation (2.7). The interaction parameters value are summarized in Table 2.1.

Their results of Fe-S-Si system agreed with those obtained by Morris and Williams[9].
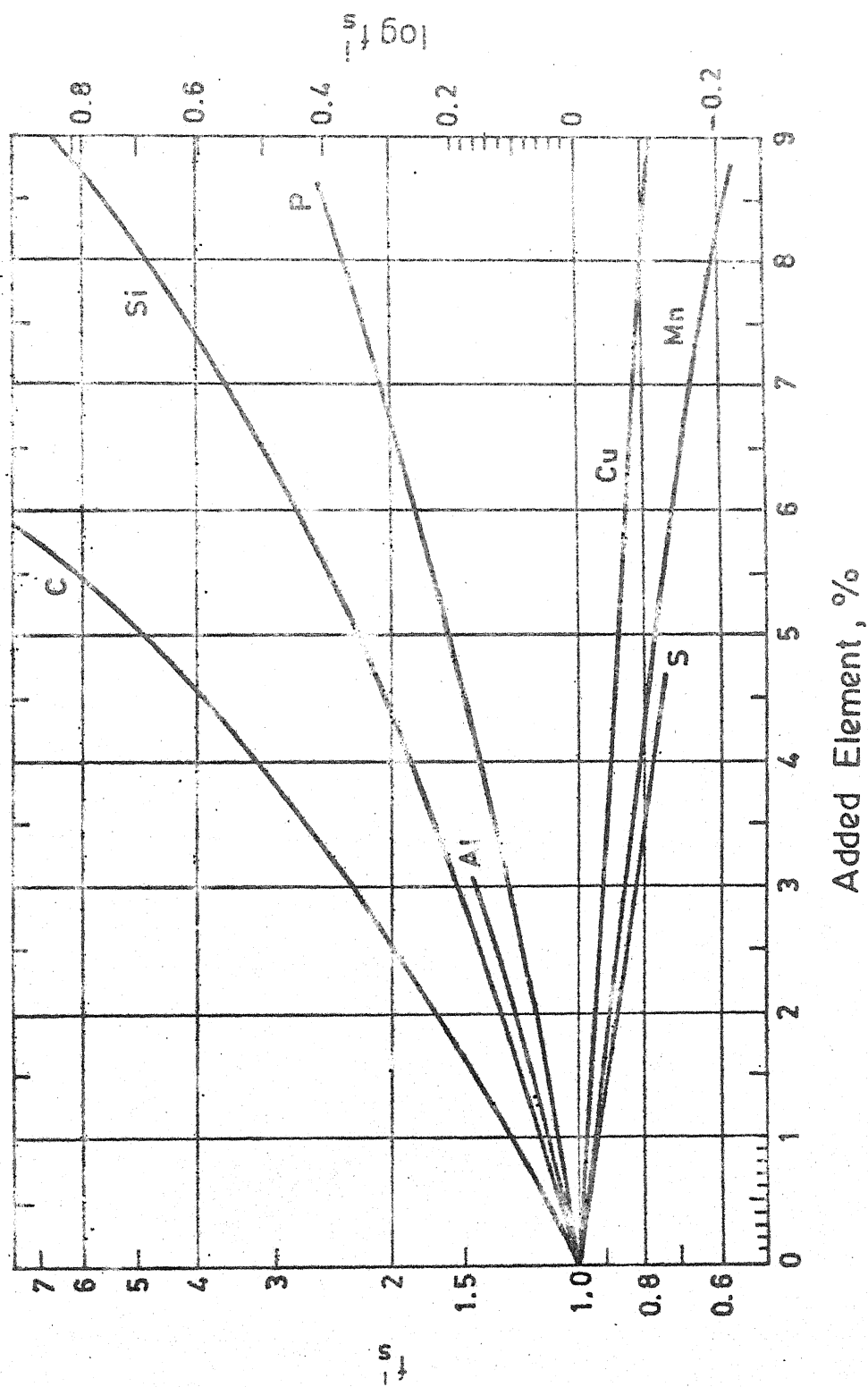
FIG. 2.3 EFFECT OF ALLOYING ELEMENTS ON ACTIVITY COEFFICIENT OF SULPHUR
IN IRON AT 1600°C. (Ref. 7)

Table 2.1 (Ref.7)

Effects of Small Concentrations of Added Substances
on Activity Coefficient of Sulphur

i = third component	$e_S^i = \partial\log f_S / \partial(\% \, i)$
C	+ 0.113
Si	+ 0.065
P	+ 0.043
Al	+ 0.054
Cu	− 0.013
Mn	− 0.025

Morris[14] investigated the activity of sulphur in
the melt containing carbon and manganese by equilibrating
with a known H_2S/H_2 ratio at $1600^{\circ}C$. His results are given
in Table 2.2. His experimental results match well with
those of Sherman and Chipman[7] as can be seen by the good
agreement in f_s values in Table 2.2.

2.4 Slag Metal Equilibrium

Hatch and Chipman[15] made an extensive scientific
study of the sulphur distribution equilibria between blast
furnace slag and metal. They melted 200 g of metal and
400 g of slag in an induction furnace, in a graphite
crucible under controlled atmosphere of carbon monoxide.
Constant stirring of the batch was provided using a graphite
rod.

Equilibrium was reported to have been reached in 4 to 6
hours of time depending on the viscosity, temperature and
composition of the slag. Attainment of silicon equilibrium
was reported slower than that of sulphur. Their equilibrium
data are summarised in Fig. 2.4.

Their results are often used to determine the
equilibrium sulphur distribution ratio (% S) /[% S] at
different composition of the slag for comparison with actual
values obtained in the iron making and steel making conditions.
Calculated sulphur distribution ratios from the equilibrium
data at different $\dfrac{CaO + MgO}{SiO_2 + Al_2O_3}$ ratios are given in Fig. 2.5.

Table 2.2 (Ref.14)

Comparison of Values of f_s Obtained by Morris with the
Calculated Values Using Data of Sherman and Chipman

Temp. °C	$\dfrac{H_2S}{H_2} \times 10^3$	C Pct	Mn Pct	S Pct	f_s (Morris)	$f_s = f_s^C f_s^S f_s^{Mn}$ (Calculated)
1600	2.36	0.0	2.2	1.04	0.90	0.83
1600	2.40	2.2	1.8	0.54	1.77	1.47
1600	2.42	4.0	2.8	0.29	3.32	2.63
1600	2.37	Saturated	2.8	0.17	5.55	5.46
1500	2.40	Saturated	2.4	0.19	5.84*	—
1400	2.34	Saturated	1.0	0.20	6.50*	—

* Recalculated by using equation (2.13) and Morris's data.
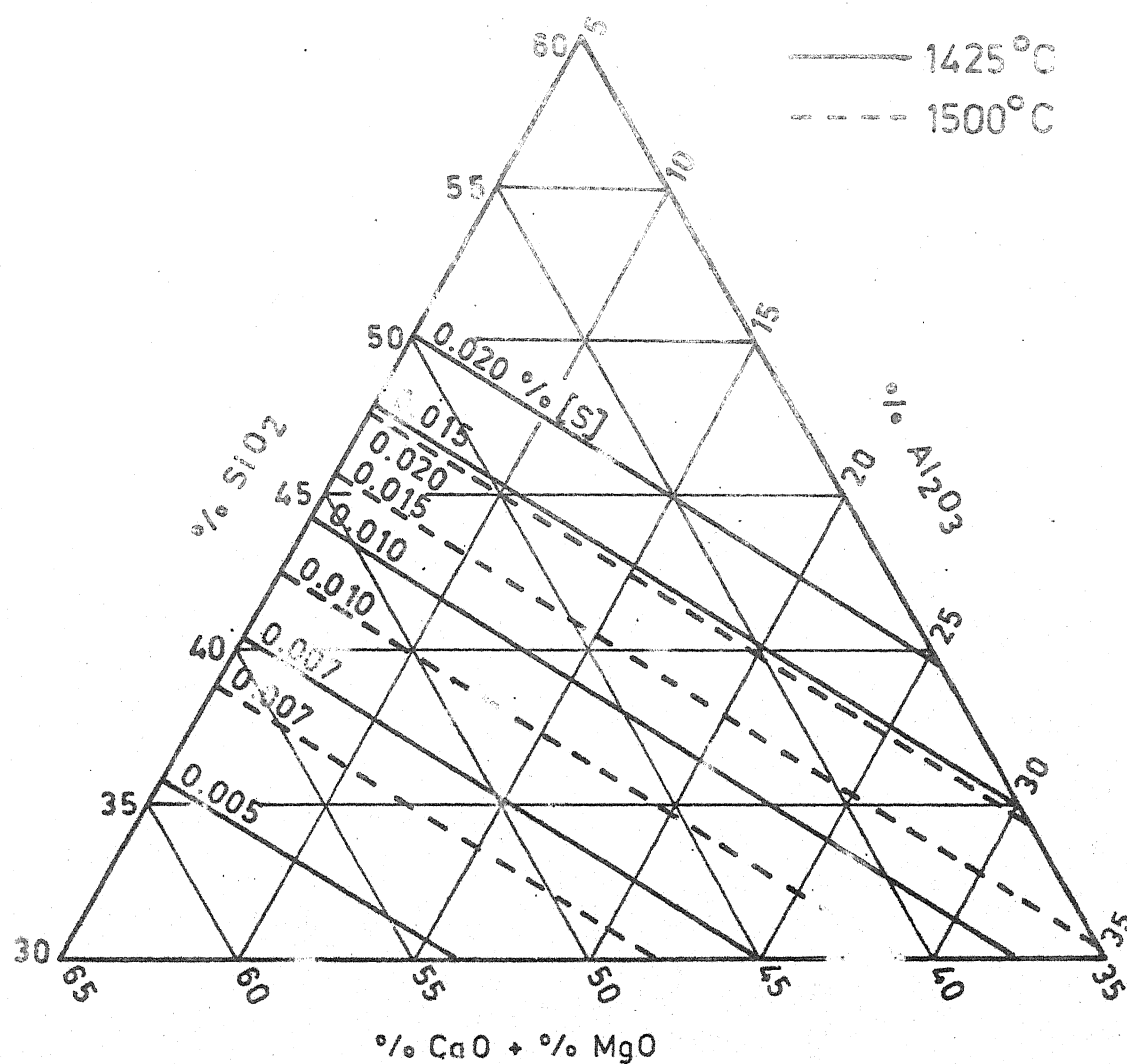
FIG. 2 4 METAL ISO-SULPHUR LINES FOR 1.5 % SULPHUR SLAGS AT 1500°C AND 1425°C. (SLAG. COMPOSITION IN WEIGHT %). (Ref. 15)
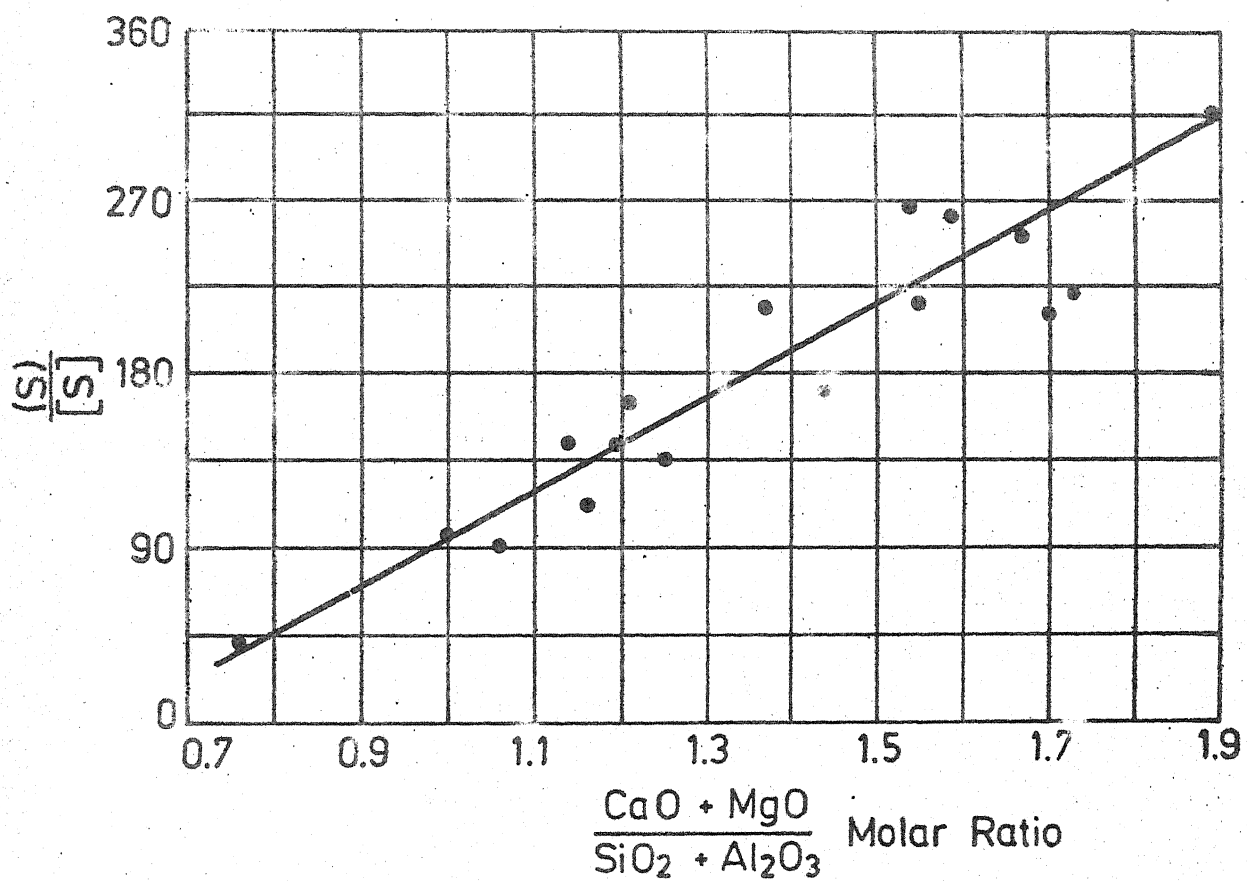
FIG.2.5 EFFECT OF $\dfrac{CaO + MgO}{SiO_2 + Al_2O_3}$ ON DESULPHURIZATION AT 1500°C. (Ref. 15)

2.5 Sulphur Reactions and Sulphur Control in Blast Furnace

Many studies are reported in the literature to enhance understanding of the sulphur reactions occuring in iron and steel making processes[16-25]. Over all sulphur transfer between slag and metal can be written as follows;

$$[FeS] + (CaO) = (CaS) + (FeO) \qquad (2.21)$$
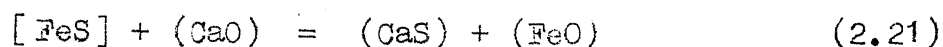
The equilibrium constant for reaction (2.21) can be expressed as follows;

$$K_{2.21} = \frac{(a_{CaS})\,(a_{FeO})}{[a_{FeS}]\,(a_{CaO})} \qquad (2.22)$$

where a_{CaS}, a_{FeO}, a_{CaO}, a_{FeS} represent the activity of CaS, FeO, CaO in the slag phase and that of FeS in the metal phase respectively.

FeO in slag can further combine with carbon or silicon in iron to give CO gas or SiO_2 in slag. The over all sulphur transfer reaction in presence of carbon can thus be written as follows[26];

$$CaO(s) + \underline{S}(1\ Pct) + C(gr) = CaS(s) + CO(g) \qquad (2.23)$$
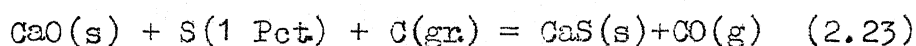
The equilibrium constant K_s for reaction (2.23) is written as follows;

$$K_s = \frac{a_{CaS}}{a_{CaO}[Pct.\ S]f_s} \times \frac{P_{CO}}{a_C} \qquad (2.24)$$

where f_s is the activity co-efficient of sulphur in the melt and it is believed to be around 7 for carbon saturated iron, a_C is activity of carbon in melt and may be taken as unity for

carbon saturated iron, p_{CO} is partial pressure of CO. The temperature dependence of the equilibrium constant K_s is determined by finding the standard free energy change of the reaction (2.23) by knowing the free energy of formation of each species and is given by;

$$\text{Log } K_s = - \frac{6010}{T} + 5.935 \qquad (2.25)$$

Data on standard free energy of solution and formation of the oxides and sulphides are given in Tables 2.3 and 2.4. The activities of CaS and CaO relative to pure solids may be represented in terms of their mole fraction and activity co-efficients;

$$\frac{a_{CaS}}{a_{CaO}} = \frac{56}{32} \times \frac{(Wt.Pct. S)}{(Wt.Pct.CaO)} \frac{\gamma_{CaS}}{\gamma_{CaO}} \qquad (2.26)$$

Simplifying equation (2.24) for carbon saturated iron in a blast furnace,

$$\frac{(Wt.Pct.S)}{[Wt.Pct. S]} p_{CO} = 4[\frac{\gamma_{CaO}}{\gamma_{CaS}}] (Wt.Pct.CaO) 10^{- \frac{6010}{T} + 5.935}$$

$$(2.27)$$

Values of $\gamma_{CaO}/\gamma_{CaS}$ ratio at different $\frac{CaO}{SiO_2}$ ratio of the slag are taken from the work of Sharma and Richardson[27] and the equation (2.27) is plotted in Figure 2.6. In the bosh region of the blast furnace CO content of the gas is around 35 Pct.and p_{CO} will be very close to 1 atm. At temperature of 1500°C at the bosh, the sulphur distribution ratio,

Table 2.3

Standard Free Energy of Solution of Various
Elements in Liquid Iron

$M(\text{pure}) = M$ (1 percent solution, Hypothetical)

(Ref. 29)

Element, State	ΔG^{o} Cal
$C(gr) = \underline{C}(\text{Wt}\%)$	$5,100 - 10.00\ T$
$Mn(l) = \underline{Mn}(\text{Wt}\%)$	$- 9.11\ T$
$\frac{1}{2}O_2(g) = \underline{O}(\text{Wt}\%)$	$-28,000 - 0.69\ T$
$Si(l) = \underline{Si}(\text{Wt}\%)$	$-28,500 - 6.09\ T$
$\frac{1}{2}S_2(g) = \underline{S}(\text{Wt}\%)$	$-31,520 + 5.27\ T$

Table 2.4

Standard Free Energies of Formation of Compounds
at Steel Making Temperatures
Ref. 29.

$$\Delta G^o = A + BT \text{ Cal.}$$

Reaction	Temp.Range ^{o}K	(A)	(B)	$\pm$KCal.
$\underline{C}(\%) + \underline{O}(\%) = CO(g)$	1700-2000	-5,350	-9.48	
Oxides				
$Ca(l) + \frac{1}{2} O_2(g)=CaO(s)$	1500-2000	-152,850	+25.78	1.0
$C(s) + \frac{1}{2} O_2(g)=CO(g)$	1500-2000	-28,200	-20.16	1.0
$Mn(l) + \frac{1}{2} O_2(g)=MnO(s)$	1516-2000	-97,550	+21.22	1.5
$Si(l) + O_2(g) = SiO_2$	1686-1986	-226,500	+47.50	3.0
Sulphides				
$Ca(l) + \frac{1}{2} S_2(g) = CaS(s)$	1500-1765	-132,060	+25.91	1.0
$H_2(g) + \frac{1}{2} S_2(g) = H_2S(g)$	1500-2000	-21,540	+11.73	0.5
$Fe(\gamma) + \frac{1}{2} S_2(g) = FeS(l)$	1500-1665	-27,130	+ 6.32	1.0
$Fe(\delta) + \frac{1}{2} S_2(g) = FeS(l)$	1665-1809	-26,700	+ 6.06	-
$Fe(l) + \frac{1}{2} S_2(g) = FeS(l)$	1809-2000	-29,970	+ 7.90	-
$Mn(l) + \frac{1}{2} S_2(g) = MnS(s)$	1516-1803	-69,250	+19.18	2.0
$Mn(l) + \frac{1}{2} S_2(g) = MnS(l)$	1803-2000	-63,100	+15.77	2.0
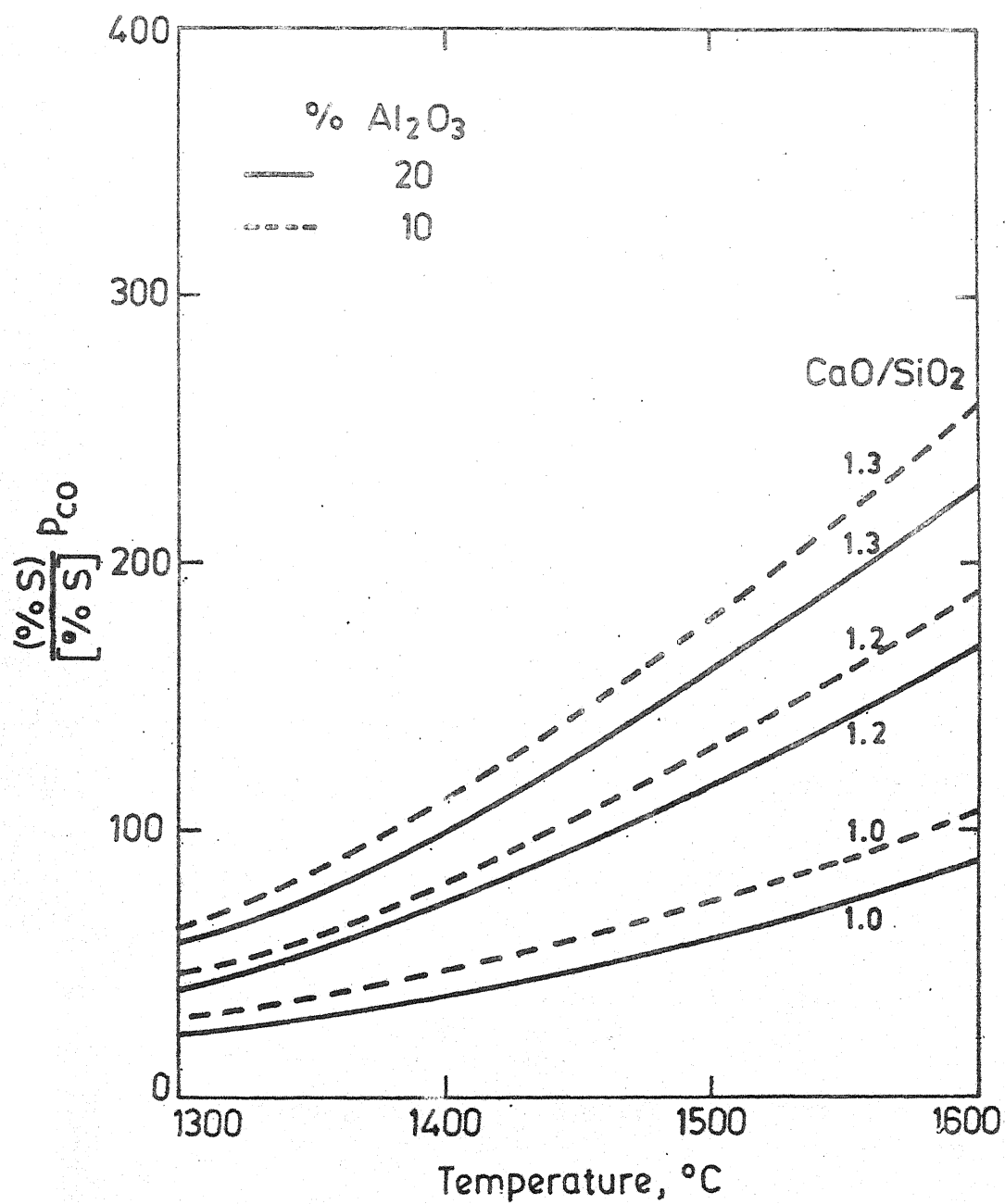
FIG. 2.6 VARIATION OF $\dfrac{(\% \, S)}{[\% \, S]} \, p_{co}$ WITH TEMPERATURE.

i.e. $\dfrac{(S)}{[S]}$ should be above 100 for $\dfrac{CaO}{SiO_2}$ ratio greater than 1.2, compared to actual range of 20 to 50 in modern blast furnaces. If p_{CO} is taken to be 2-4 atm. the calculated values will agree well with the actual value. p_{CO} values of 2-4 atm. may exist in the hearth of the furnace at slag metal interface where CO evolved is not diluted by N_2 in the blast.

It may thus be concluded that slag - metal equilibrium is more or less reached in the hearth of blast furnace where small metal droplets trickle down a depth of molten slag layer. This equilibrium is not easily reached in the bosh. Similar arguments also explain the observed silicon and manganese levels in modern blast furnaces where slag metal equilibrium may be assumed to be prevailing in the hearth at p_{CO} values of 3-4 atm.

Some confusion exists in the literature as silicon and manganese reduction reaction are believed to be sluggish and sulphur equilibrium is not believed to reach equilibrium. These arguments are valid if p_{CO} is taken to be around 1 atm. only. Many workers therefore proposed different mechanisms

for transfer of sulphur from metal to the slag phase[26,28]. In the slag sulphur may be present as S^{--} ions, oxygen as O^{--} and Mn as Mn^{++} and so on. Electrical neutrality of the slag must be maintained for any reaction to proceed. Thus King and Ramachandran[28] demonstrated that transfer of sulphur from the metal to slag must be accompanied by the transfer of Si and Mn to the slag. Turkdogan[26] analysed large plant data and found more agreement for the sulphur and manganese coupled reaction, i.e.

$$[Mn] + [S] + (CaO) = (CaS) + (MnO) \qquad (2.28)$$

$$K_{2.28} = \frac{a_{CaS} \; a_{MnO}}{f_{Mn} \; f_s [Mn][S] \; a_{CaO}} \qquad (2.29)$$

$$\log K_{2.28} = \frac{9080}{T} - 4.965 \qquad (2.30)$$

The plot of $[Mn] / (MnO)$ versus $\frac{(S)}{[S]}$ at $1500^{\circ}C$ shown in Figure 2.7. Reaction (2.28) will be equivalent to reaction (2.23) if [Mn] in metal is assumed to be governed by the following reaction;

$$(MnO) + C(gr.) = [Mn] + CO(g) \qquad (2.31)$$
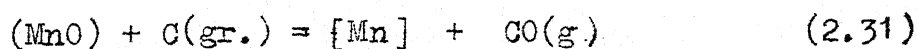
As explained earlier p_{CO} must be taken to be 3-4 atm. in
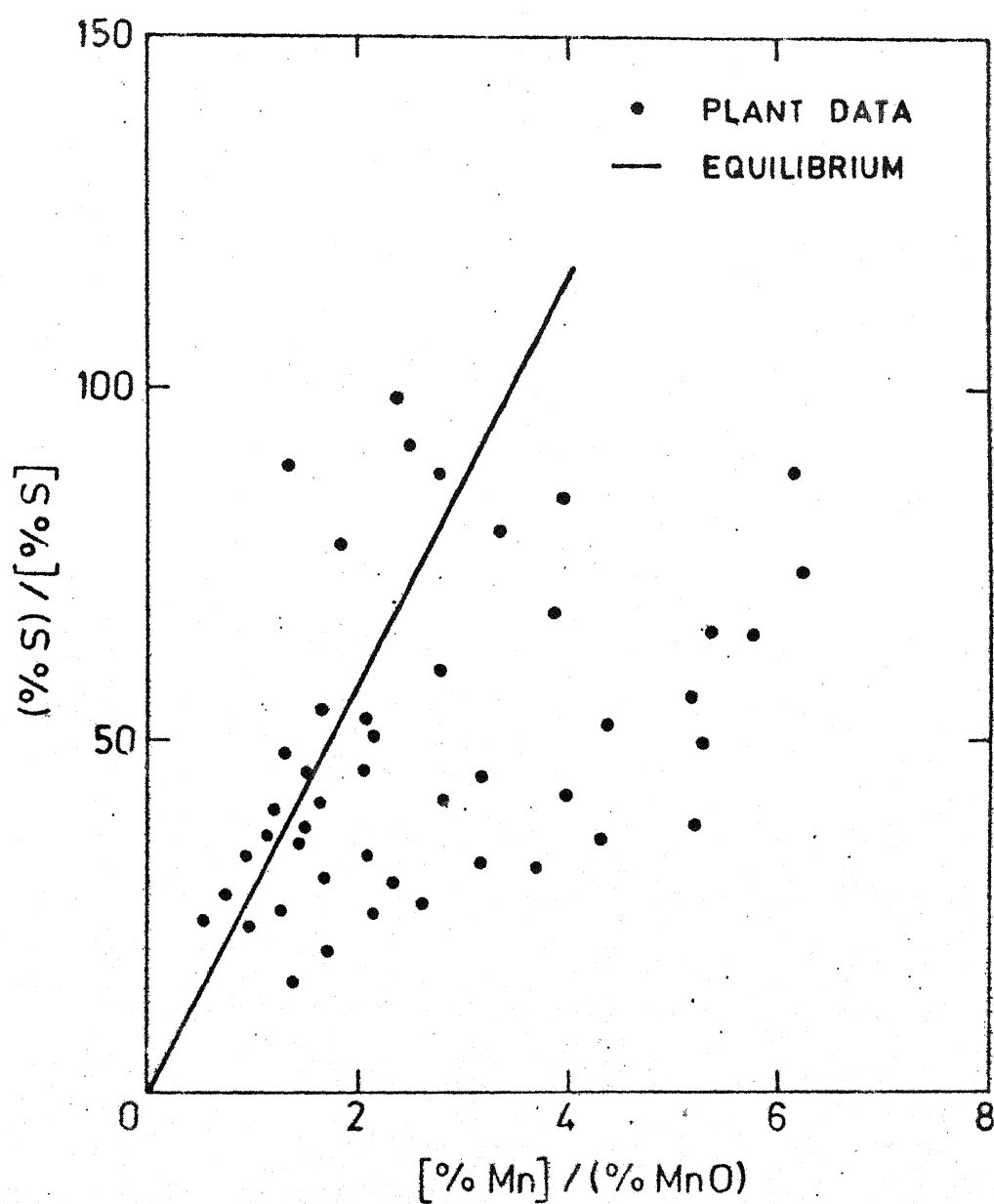
FIG. 2.7 EQUILIBRIUM SULPHUR AND MANGANESE DISTRI-
BUTION RATIOS AT 1500°C COMPARED WITH PLANT
DATA. (Ref. 26)

order to calculate the theoretical [Mn] content of metal for better comparison with the actual data for a blast furnace.

Similarly, the reaction involving silicon is represented by;

$$CaO\ (s) + \frac{1}{2} Si(1\ Pct) + \underline{S}\ (1\ Pct) = CaS\ (s) + \frac{1}{2} SiO_2(s)$$

$$(2.32)$$
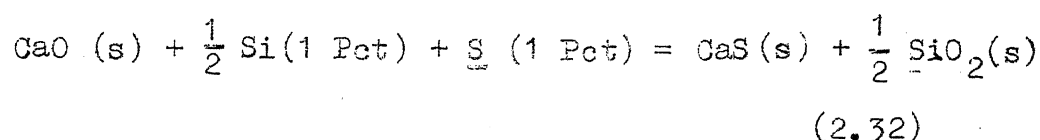
The temperature dependence of the equilibrium constant

$$K_{Si-S} = \frac{(a_{CaS})\ (a_{SiO2})^{1/2}}{(a_{CaO})\ [a_{Si}]^{1/2}[a_S]}$$ can be determined as follows,

$$Log\ K_{Si-S} = + \frac{9865}{T} - 4.52 \qquad (2.33)$$

$\frac{(S)}{[S]}$ ratio is plotted versus $\frac{[Si]}{(SiO_2)}$ in Figure 2.8.

In some blast furnaces operated with high ash coke; S, Si, Mn reactions may not reach equilibrium with respect to carbon due to a different mechanism for the reduction of SiO_2 i.e. due to formation of SiO, SiS vapors at the tuyere of a blast furnace[26,36]. The coupled reactions described by equations (2.28) and (2.32) may however still try to reach equilibrium in the hearth.

'Mn' content of metal will be governed by the following reaction;

$$[Si] + 2(MnO) = 2[Mn] + (SiO_2) \qquad (2.34)$$
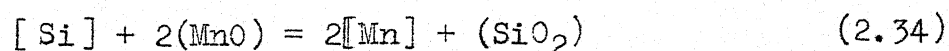
$$K_{Mn-Si} = \frac{(a_{SiO2})\ [a_{Mn}]}{[a_{Si}]\ (a_{MnO})^2} \qquad (2.35)$$
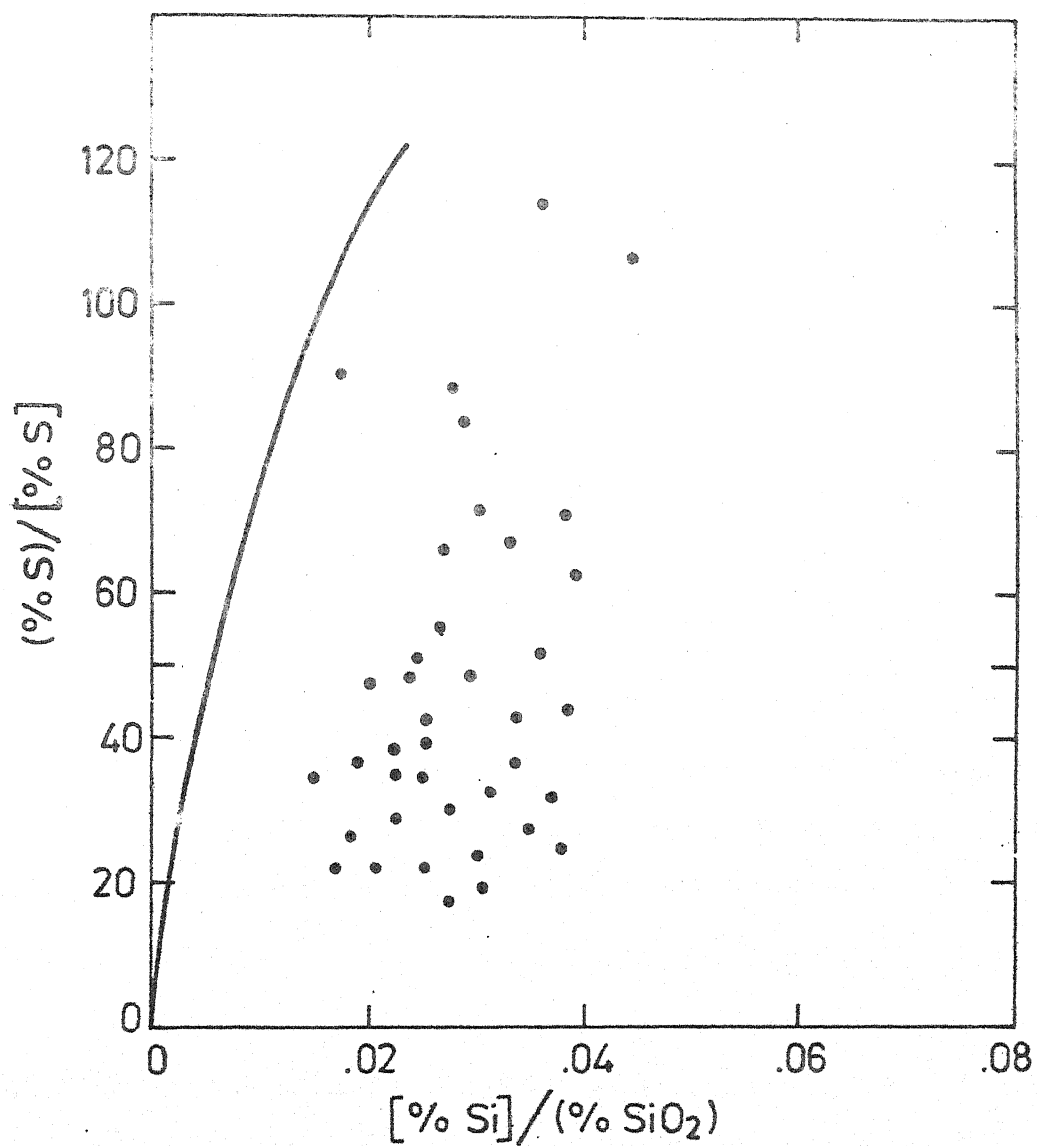
FIG. 2.8 EQUILIBRIUM SULPHUR AND SILICON DISTRIBUTION
RATIOS AT 1500°C, COMPARED WITH PLANT DATA.
(Ref. 26)

$$\text{Log } K_{Mn-Si} = \frac{1570}{T} + 0.89 \qquad (2.36)$$

In such cases silicon replaces carbon as a reducing agent for the reduction of MnO, Cr_2O_3, TiO_2 etc.

2.6 Effect of Temperature on Solutbility of Sulphur in Presence of Mn

2.6.1 Laboratory studies

Oelsen[6] studied the solubility of MnS in carbon saturated blast furnace iron and reported that the solubility of MnS decreased in the melt with decreasing temperature as shown in Figure 2.9. 'Si', and 'P' content of the blast furnace iron were not specified by Oelsen.

Morris[14] studied Mn-S equilibrium in Fe-C alloys by stepwise addition of manganese. His results are summarised in Figure 2.10. Morris reported that [Mn%][S%] product was nearly constant over a concentration range of 1 to 7 Pct. Mn, at a fixed temperature. The average values of [Mn%][S%] products were 0.05 and 0.26 at temperatures of 1200°C and 1400°C respectively, matching well with Oelsen's work. At 1600°C the [Mn%][S%] product increased from 0.8 at 1 pct. Mn to 1.2 at 7 pct. Mn. Where as according to Oelsen's [Mn%][S%] product increased from 0.57 at 1 pct. Mn to 0.92 at 4 pct. Mn, at the same temperature.

Morris concluded from his data that manganese alone could not be an efficient desulphuriser except at temperatures
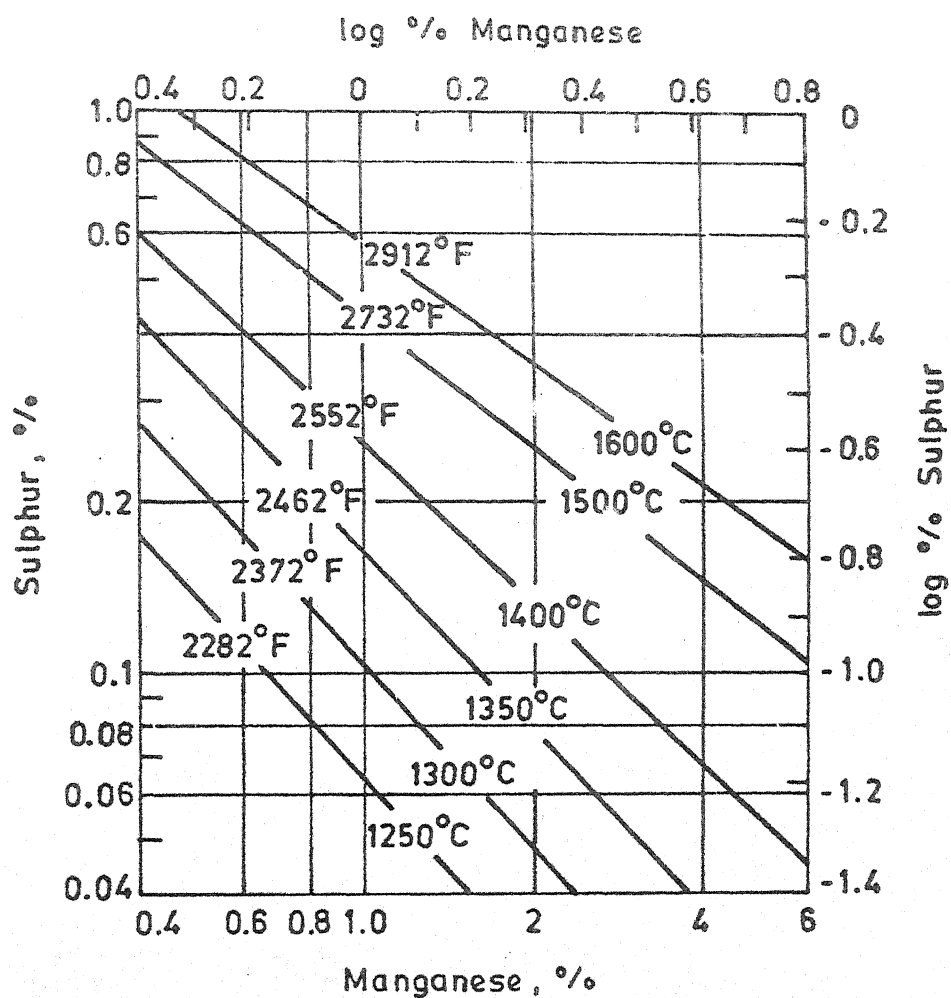
FIG. 2.9 EFFECT OF MANGANESE ON SOLUBILITY OF MANGANESE SULFIDE IN HOT METAL. (Ref. 6)
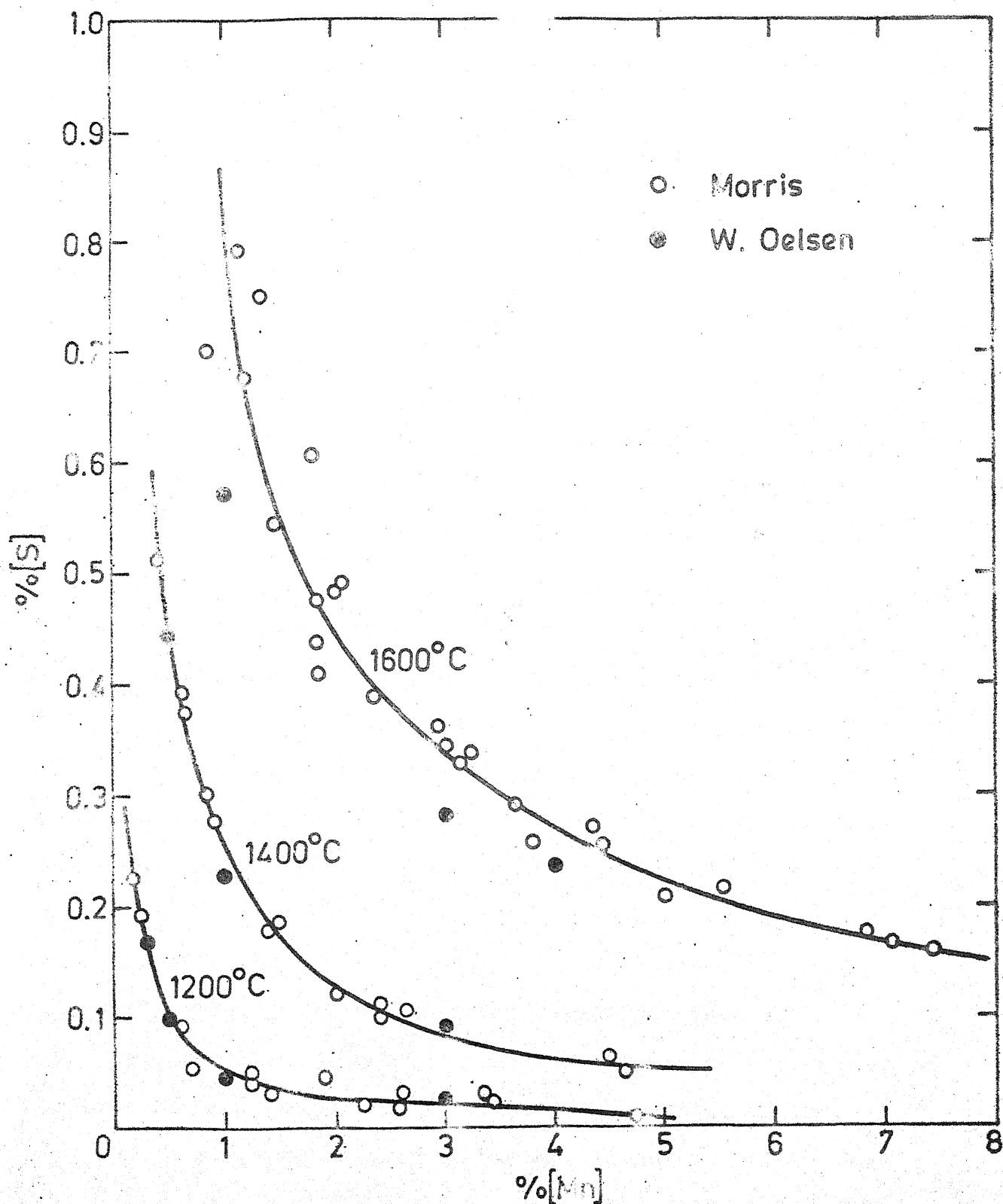
FIG. 2.10 EFFECT OF MANGANESE ON THE SULPHUR CONTENT OF CARBON SATURATED MELTS OF IRON IN EQUILIBRIUM WITH MnS-FeS SLAG. (Ref. 14)

below the normal operating range. However he predicted that in the presence of an oxide slag, manganese could be more effective as a desulphuriser than indicated in his results, due to lowering of the activity of manganese sulphide in the slag. This aspect of decreasing a_{MnS} (i.e. activity of MnS) in slag was not studied by him.

2.6.2 Industrial data

If initial sulphur level in iron is high, and the temperature of metal decreases during the transit of the ladle, some sulphur may precipitate out as MnS. Corresponding drop in Mn content of metal may be too small to be noted as the concentration of sulphur does not normally exceed 0.05 Pct. Drop in sulphur may be of the order of 0.01 to 0.02 Pct. and it can account for 30 to 50 Pct. of sulphur removal in the slag. Rourkela steel plant has been producing the blast furnace metal with Mn contents of 1.5 to 2.5 Pct. consistently over the last many years. There is a substantial difference in sulphur levels of the samples taken at the time at blast furnace tapping and at the time of taking out metal from the mixer. Typical Mn and S levels in blast furnace iron and mixer iron are plotted in Figure 2.11 for comparison purposes. More details regarding metal temperature, mixer slag composition etc. are not available. Slag is likely to contain CaO, SiO_2, Al_2O_3, MnO, FeO, and sulphur as its origin may be due to the carry over slag from the blast furnace, oxidation of metal in the mixer, addition of coke breeze to the top layer of iron ladle, formation of MnS due to lowering of temperature etc.
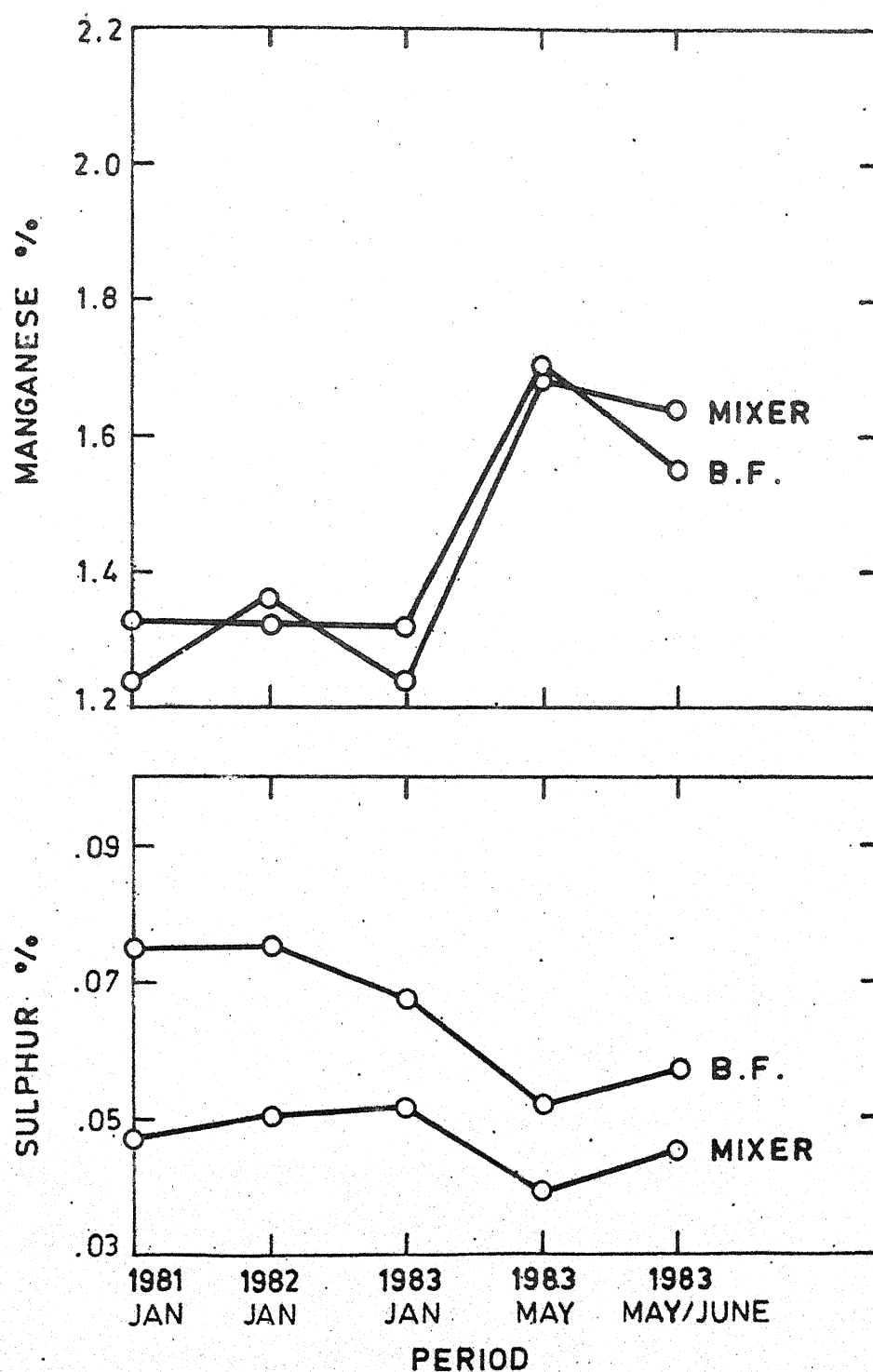
FIG. 2.11 INDUSTRIAL DATA ON MANGANESE AND SULPHUR
LEVELS IN BLAST FURNACE IRON AND MIXER IRON.
(SOURCE - ROURKELA STEEL PLANT)

A typical mixer slag composition is given below;

$CaO = 20\%$, SiO_2, 40%, $Al_2O_3 = 20\%$

$FeO = 5\%$, $S = 0.70\%$ and the balance may be Fe, MnO, MgO etc. This slag must be removed carefully as to take full advantage of sulphur removal as MnS, otherwise sulphur would revert to metal under oxidising condition in the LD steel making where metal temperature may rise to $1600^{\circ}C$. Rourkela Steel Plant has acquired 3 slag racking machines for this purpose.

Mn may not act as desulphuriser alone to attain the lower 'S' levels in metal and it may be necessary to add desulphurising agents such as CaO, CaC_2, Na_2CO_3 etc. Rourkela steel plant has incorporated the facility of external desulphurisation where CaC_2 powder is injected to metal using coated lances and air as carrier. Other plants like Bhilai, Bokaro may also have such facilities in their expansion pro-grammes. It is not known how the presence of Mn in metal will influence the desulphurisation capacity of these agents. Results of the laboratory investigations reported in the present work may be helpful in better understanding of the role of Mn in the external desulphurisation of iron.

CHAPTER III

PLAN FOR PRESENT WORK

From the available literature and the industrial data,
practical importance of 'Mn' and 'S' reactions in blast furnace
iron can not be under estimated. However, few scientific
studies are available in the temperature range of $1200^{\circ}C$ to
$1400^{\circ}C$, which may usually occur in the transit of metal from
the blast furnace to the mixer and during external desulphuri-
sation of iron. The present work was aimed at making such
studies under controlled conditions in the laboratory. The
work may be described as follows;

(1)   The literature survey comprising the critical evaluation
        of the necessary thermodynamic data.

(2)   Laboratory experiments to establish relationships between
        'Mn' and 'S' in the Fe-C alloys in temperature range
        of $1200\text{-}1400^{\circ}C$ with or without any slag additions. This
        included fabricating a silicon carbide furnace, making
        Fe-C alloys, melting the alloy under argon atmosphere
        in a graphite crucible, drawing samples with a quartz
        tube and careful analysis of sulphur and manganese in
        the laboratory.

(3)   The effect of 'Mn' in metal on the desulphurising
        power of the oxide slags was studied by making synthetic
        slag of $CaO\text{-}SiO_2\text{-}Al_2O_3$ in the laboratory and equili-
        brating the melt at $1400^{\circ}C$ with those slags for 4-6
        hours of duration. Samples were either drawn from the

melt or taken from the solidified mass in the crucible
after the duration of experiment. Pure lime was also
used as a desulphuriser in some experiments for
comparison purposes.

(4) Evaluation of the laboratory data by developing
suitable theoretical and multicomponent models and
by comparison with the other published data in such
system.

(5) Collection and evaluation of industrial data to
signify the practical importance of the present work.

CHAPTER IV

RESULTS OF THEORETICAL CALCULATIONS

4.1 Evaluation of Reported Thermodynamic Data

As mentioned in Section 2.6.1, solubility of sulphur in iron carbon alloys decreases with addition of Mn to the alloy at a constant temperature and with decrease in temperature at a constant Mn level. It is also possible to determine theoretically the sulphur content of metal as function of temperature and Mn content of metal if the corresponding data on standard free energy of formation of MnS and the activity co-efficient of 'Mn' and 'S' in metal are known.

4.1.1 Standard free energy of formation

The standard free energy change for the following reaction can be determined from the values given in Tables 2.3 and 2.4.

$$\underline{Mn} \ (Wt\% \ ) + \underline{S} \ (Wt\% \ ) = MnS(1) \tag{4.1}$$
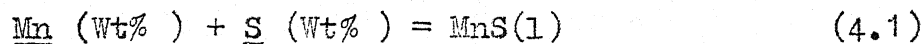
$$\Delta G^{o}_{4.1} = -31,580 + 19.61 \ T \ Cal. \tag{4.2}$$

$\Delta G^{o}_{4.1}$ is valid in the temperature range $1803^{o}-2000^{o}K$ The equilibrium constant $K_{4.1}$ for the reaction (4.1) is given by;

$$K_{4.1} = \frac{a_{MnS}}{f_{Mn} \ f_{s} \ [Wt\% \ Mn \ ][\ Wt\% \ S \ ]} \tag{4.3}$$

and $\log \dfrac{a_{MnS}}{f_{Mn} \, f_s \, [\, wt\% \, Mn][\, wt\% \, S\,]} = \dfrac{6902.7}{T} - 4.28$ (4.4)

In the temperature range of $1516^\circ - 1803^\circ K$,

$$\underline{Mn}(wt \;\;) + \underline{S} \; (wt\% \;) = MnS(s) \qquad\qquad (4.5)$$
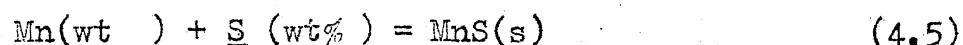
and $\quad \Delta G^0_{4.5} = -37,730 + 23.02 \; T \; cal \qquad\qquad (4.6)$

where, a_{MnS} is the activity of MnS is slag, f_{Mn} and f_s are the activity coefficients of $[\,Mn\,]$ and $[\,S\,]$ in the melt. The standard states of mangane and sulphur are chosen to be 1 wt pct in the solution and their activity coefficients approach unity when the concentrations of all the solutes tend to be zero.

4.1.2 <u>Activity coefficient of sulphur</u>

For finite concentrations of solutes, one has to know the value of interaction parameters to determine the activity coefficient as follows;

$$\log f_s = \sum_{i=1}^{n} e_s^i \; (wt\% \, i \,) \qquad\qquad (4.7)$$

Values of interaction parameters have been determined by various workers[7,10], by equilibrating the melt with H_2 and H_2S gas mixtures and determining the sulphur content of the metal. Table 4.1 summarises the interaction parameters at $1600^\circ C$.

Table 4.1

Values of Interaction Parameters at $1600^{\circ}C$

Solute j	e_s^j	Ref.	e_{Mn}^j	Ref.
C	0.11	30		
	0.12	12		
	0.15	10	−0.07	30
	0.24	31		
Si	0.063	30		
			0.0	30
	0.066	31		
Mn	−0.026	30	0.0	32
			−0.0029	30
P	0.045	31		
			−0.0035	30
	0.029	30		
S	−0.028	30, 31	−0.048	30
			−0.043	31

For carbon saturation, pct carbon is very high compared to other solutes and because of this carbon-sulphur interactions are important, e_S^C values should be thus known more accurately than other values. Unfortunately there is scatter in the data shown in Table 4.1. Sources of discrepancies in e_S^C values have already been discussed in Chapter 2.

Young and Clark[33] recently established that e_S^C value of 0.16 ± 0.01 at $1600^{\circ}C$ gives the best approximation to the actual plant data. This is closer to the average value of 0.15 from the data of Morris and Buehl[10].

4.1.3 Activity coefficient of manganese

It is generally assumed that most alloying elements have no significant effect on the ideal behaviour of manganese in steel, but carbon is known to decrease the activity of manganese in iron-carbon-manganese alloys[34,35]. The variation of activity coefficient f_{Mn} with composition in liquid Fe-C-Mn alloys at $1540^{\circ}C$ is shown in Figure 4.1.

From Figure 4.1 it is seen that for carbon saturated iron containing 3 pct Mn (broken line $X_{Mn}=0.03$), f_{Mn}^C value is around 0.95. Turkdogan has estimated the activity coefficient of Mn in carbon saturated liquid iron to be 0.8.

In the present work f_{Mn} is assumed to be 0.8, for the carbon saturated melt in the absence of more accurate data.
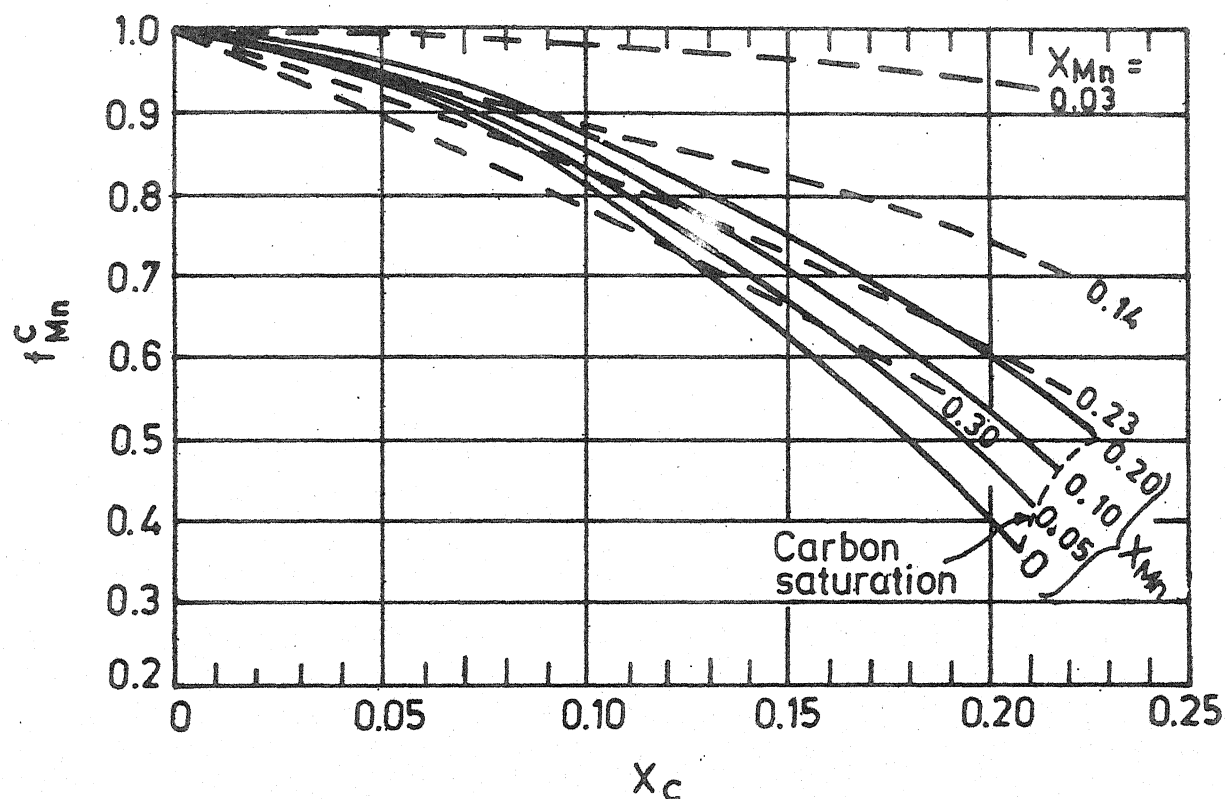
FIG. 4.1 VARIATION OF THE ACTIVITY COEFFICIENT, f^C_{Mn}, WITH COMPOSITION IN LIQUID IRON-CARBON-MANGANESE ALLOY AT 1450°C. (Ref. 34, 35) (FULL CURVE Ref. 35 AND BROKEN CURVE Ref. 34)

4.2 Determination of Activity Coefficients of Sulphur and Manganese at Temperatures of 1200°C to 1500°C

Melting point of iron decreases in presence of carbon. For carbon saturated iron, melting point may be as low as 1150°C. Most of the thermodynamic data is however obtained at 1600°C with reference to the steel making conditions. It is necessary to know the values of activity coefficients at lower temperatures of 1200° - 1500°C if the solubility of sulphur is to be calculated in iron-carbon alloys at temperatures less than 1600°C. In the present work, a regular solution model is applied to extrapolate the interaction parameters.

The expression for the standard free energies of formation given in Table 2.3 - 3.4 are assumed to be valid at these temperatures though they might have been derived from the experimental data in the temperature range 1500°-1600°C.

For a regular solution the quantity $RT \ln \gamma_i$ should not change with temperature, where R is the gas constant, T is temperature in K and γ_i is the activity coefficient of the solute 'i' in the Raoultian scale.

The Raoultian and Henrian interaction coefficients are defined as follows;

$$e_i^j = \frac{\partial(\ln \gamma_i)}{\partial(X_j)} \qquad X_i, X_j \to 0 \qquad (4.8)$$

$$e_i^j = \frac{\partial(\log f_i)}{\partial(\text{wt}\% \ j)} \qquad \text{wt}\% \ i, \ j \to 0 \qquad (4.9)$$

The term e_i^j corresponds to the reference state of the pure substance, and concentrations are expressed in atom or mole fractions. The term e_i^j is applicable to the infinitesimal dilute solution as the reference state and concentrations are expressed in weight percents.

As $RT \ln \gamma_i$ is constant for a regular solution ; one can write the following;

$$RT_1 \; e_i^j(1) = RT_2 \; e_i^j(2) \tag{4.10}$$

where $e_i^j(1)$ and $e_i^j(2)$ are Raoultian interaction parameters at temperatures T_1 and T_2 respectively. It is also known that, the two types of interaction parameters are related as follows[31];

$$e_i^j = 230 \frac{M_j}{M_1} e_i^j + \frac{M_1 - M_j}{M_1} \tag{4.11}$$

M_j, M_1 are the molecular weights of the solute 'j' and the solvent iron.

$$\text{Let} \quad \frac{M_1 - M_j}{M_1} = c_0 \tag{4.12}$$

On simplification equation (4.11) can be written as;

$$\frac{1 - \dfrac{c_0}{e_i^j(1)}}{1 - \left[\dfrac{T_2}{T_1} x \dfrac{c_0}{e_i^j(1)}\right]} = \frac{T_1}{T_2} \frac{e_i^j(1)}{e_i^j(2)} \tag{4.13}$$

Henrian interaction coefficient $e_i^j(1)$ at temperature T_1 (i.e. $1873^\circ K$) is known from literature (Table 4.1). So at any other temperature T_2; $e_i^j(2)$ i.e. the interaction coefficient at the desired temperature can be calculated by using equation (4.13).

The results of the calculations of interaction parameters are summarised in Table 4.2. Using these values f_s can be determined at any temperature for any batch composition with the help of equation 4.7 and f_{Mn} can be determined using the following.

$$\log f_{Mn} = \Sigma \, e^i_{Mn} \, (wt\% \, i) \tag{4.14}$$

Value of f_{Mn} is, however, assumed to be 0.80 for carbon saturated iron at all temperatures.

4.3 Solubility of Sulphur in Fe-Mn-S System at 1600°C

4.3.1 Determination of f_s and f_{Mn} values

The f_s and f_{Mn} values are determined by taking the interaction parameter values as given in Table 4.1 and applying equation (4.7) and (4.14).

4.3.2 Determination of equilibrium sulphur levels

Equilibrium sulphur level of the metal at 1600°C is calculated by using equation (4.4). The procedure of calculation is discussed below. In the first case the slag is assumed to consist of only manganese sulphide so that a_{MnS} can be taken as unity.

For a particular Mn level in the batch S level is first assumed or estimated approximately f_s and f_{Mn} values are then calculated by using equation (4.7) and equation (4.14); and the sulphur level is recalculated using equation (4.4).

Table 4.2

e_i^j Values at $1200^\circ C - 1600^\circ C$

Temp. $^\circ C$	e_s^c	e_s^{Mn}	e_s^s
1600	+ .1500	-.0260	-.0280
1500	+ .1600	-.0270	-.0295
1400	+ .1698	-.0290	-.0309
1300	+ .1816	-.0309	-.0327
1200	+ .1950	-.0330	-.0347

The steps are repeated until the successive calculated sulphur levels are about the same.

In the second case the slag is assumed to consist of iron sulphide and manganese sulphide binary system and their behaviour is assumed to be ideal at 1600°C. From the FeS-MnS phase diagram as shown is Figure 4.2, it is seen that FeS and MnS are completely soluble in the liquid phase. Activity of FeS or its mole fraction in the slag is related to sulphur content of iron as follows ;

$$\underline{Fe} + \underline{S} = FeS \tag{4.15}$$

$$K_{4.15} = \frac{a_{FeS}}{a_{Fe} \, f_s \, [wt\% \, S]} \tag{4.16}$$

Setting a_{Fe} equal to unity

$$a_{FeS} = K_{4.15} \, f_s \, [wt\% \, S] \tag{4.17}$$

Assuming ideal behavior, $a_{FeS} = X_{FeS}$.

For the slag consisting of FeS and MnS only

$$a_{MnS} = X_{MnS} = 1 - X_{FeS} \tag{4.18}$$

where X_{FeS} and X_{MnS} are the mole fractions of FeS and MnS respectively. But from equation (4.3) ;

$$[wt\% \, S] = \frac{a_{MnS}}{f_{Mn} \, f_s \, [Mn] \, K_{4.1}} \tag{4.19}$$

By inserting equations (4.17) and (4.18) in equation (4.19) and simplifying, the sulphur level in the metal can be calculated as follows;
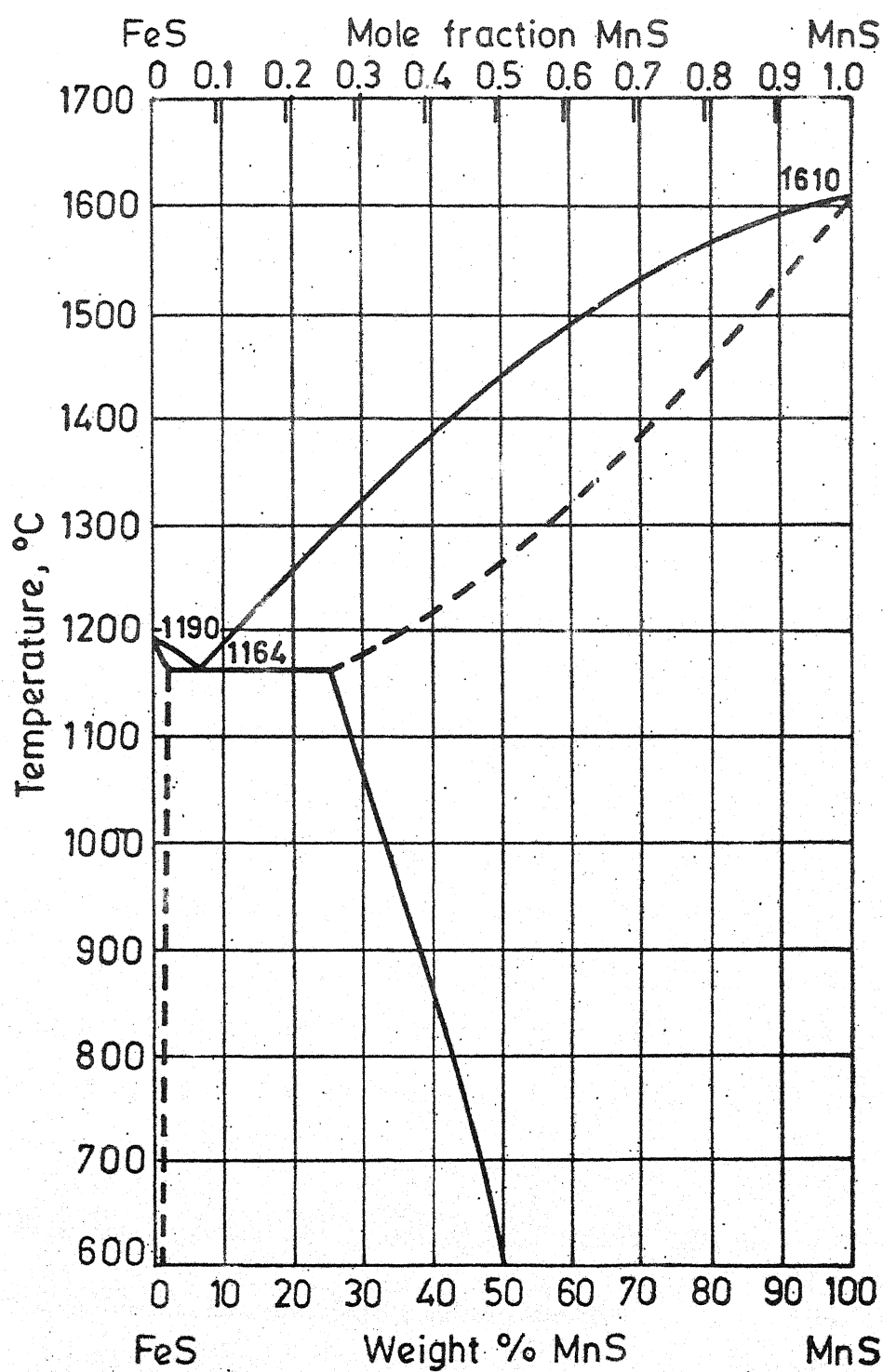
FIG. 4.2 PHASE DIAGRAM OF FeS - MnS.(Ref. 37,38)

$$[\text{wt} \% \text{S}] = \frac{1}{f_s(K_{4.15} + f_{Mn}[Mn]K_{4.1})} \qquad (4.20)$$

The values of f_s, f_{Mn} and equilibrium sulphur content are summarised in Table 4.3.

4.3.3 Comparison with published data

The calculated sulphur and manganese levels in Table 4.3 are plotted in Figure 4.3 along with the experimental data of Sherman and Chipman[7]. The calculated sulphur levels lie much above the experimental points of Sherman and Chipman[7], who determined sulphur and manganese levels in the melts after allowing them to reach equilibrium with respect to $H_2 + H_2S$ gas mixtures. It is obvious that MnS could not be formed in their experiments as sulphur content was always below the level at which MnS or FeS would precipitate out. Meyer's[39] experimental results of the equilibrium sulphur and manganese levels in the FeS+Mn = Fe+MnS system are also plotted in Figure 4.3. Sulphur levels in Meyer's experiment are found to be lower than the equilibrium values because of the presence of 4 to 6 pct. Al_2O_3 which might have lowered the values of a_{MnS} and a_{FeS} further.

4.4 Solubility of Sulphur in Fe-Mn-C-S- System

4.4.1 Solubility of carbon in iron alloys

For iron-carbon alloys it is possible to work at temperatures less than $1600^{\circ}C$. At any temperature saturated carbon level in the alloy can be calculated by using the following relationship[33]:

Table 4.3

Equilibrium[Mn] and[S]levels at $1600^{\circ}C$ in Fe-Mn-S System

Pct[Mn]	f_{Mn}	f_s	Pct[S] $a_{MnS}=1$	Pct[S] $a_{MnS}=X_{MnS}$	X_{MnS}
2.5	0.70	0.70	3.20	2.26	0.70
3.0	0.75	0.70	2.50	1.88	0.75
4.0	0.81	0.70	1.80	1.41	0.78
5.0	0.85	0.67	1.38	1.18	0.85
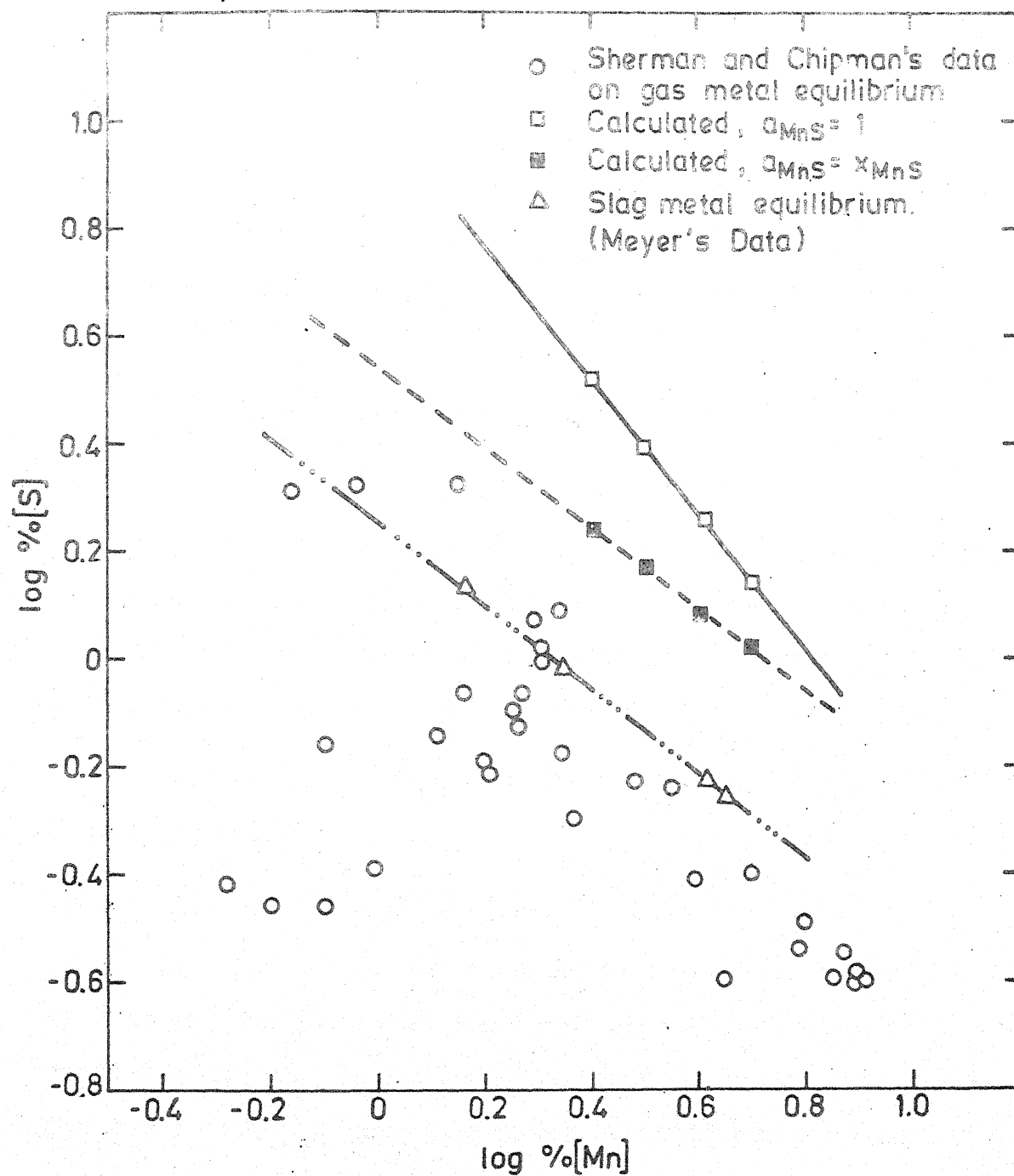
FIG. 4.3 EQUILIBRIUM [Mn] AND [S] LEVELS AT 1600°C.

$$[C]_{sat} = 1.34 + 2.54 \times 10^{-3}(T^{o}C)$$
$$-0.35[P] + 0.17 [Ti] - 0.40 [S]$$
$$+ 0.04[Mn] - 0.30[Si] \qquad (4.21)$$

where, the elements in the bracket represent their concentration in the iron alloy in wt pct.

Equation (4.21) is plotted in Figure 4.4. This shows the effect of alloying elements on carbon saturation values at different temperatures.

4.4.2 Determination f_S and f_{Mn} values

'f_S' values can be determined at $1600^{o}C$ by using equation (4.7) and the interaction parameter values reported in Section 4.1.2. At lower temperatures, interaction parameters can be calculated using equation (4.13), and the equation (4.7) can be then used to calculate the f_S value.

For carbon saturated melt f_{Mn} is assumed to be 0.8 at all temperatures.

4.4.3 Determination of equilibrium sulphur levels

Equation (4.4) can be used to determine the sulphur level at any manganese in the metal above $1530^{o}C$, whereas equation (4.6) can be used at temperatures lower than $1530^{o}C$, provided f_S and f_{Mn} are calculated by using the suitable equations as discussed earlier. The results of the calculations by taking a_{MnS} equal to unity are given in Table 4.4.
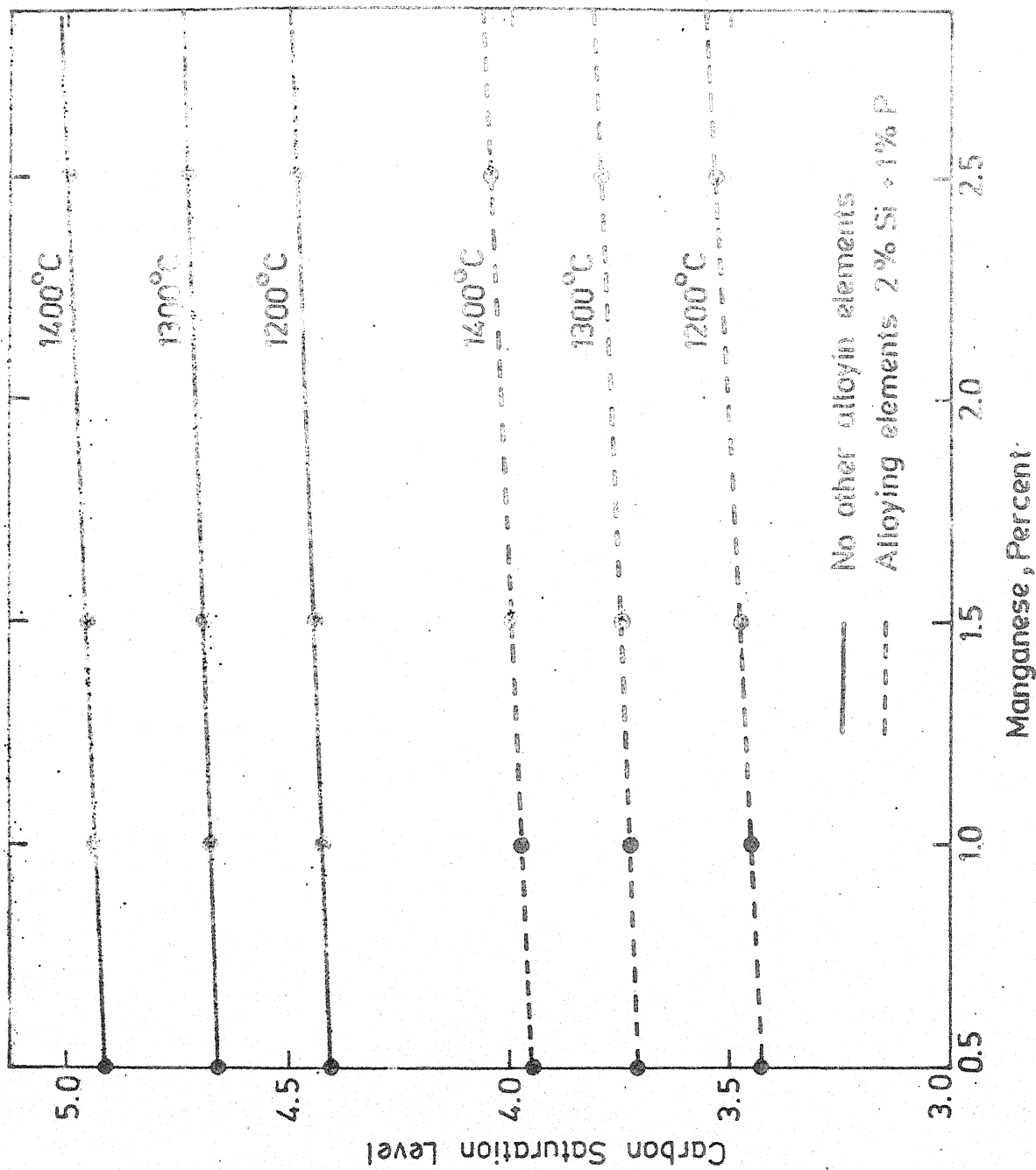
FIG. 4.4. EFFECT OF ALLOYING ELEMENTS ON CARBON SATURATION LEVEL AT DIFFERENT TEMPERATURES.

Table 4.4

Results of Theoretical Calculations of Equilibrium [Mn]
and [S] levels in Fe-C-Mn-S System at 1200º-1500ºC
(Assumption: f_{Mn} = 0.8 and a_{MnS} = 1.0)

Temp. ºC	Pct[Mn]	Pct C_{sat}	f_s	Pct [S] $a_{MnS=1}$	Pct [S] $a_{MnS}=X_{MnS}$
	0.4	4.38	7.05	0.120	0.1080
	1.0	4.41	7.00	0.048	0.0460
	1.4	4.43	6.98	0.034	-
	2.0	4.46	6.93	0.024	0.0227
1200	2.6	4.48	6.87	0.019	-
	3.0	4.51	6.83	0.017	0.0168
	3.6	4.53	6.78	0.014	-
	4.0	4.55	6.74	0.013	0.012
	0.4	4.60	6.86	0.280	0.2190
	1.0	4.66	6.80	0.112	0.1010
	1.4	4.67	6.76	0.080	-
	2.0	4.70	6.71	0.056	0.0540
1300	2.6	4.74	6.66	0.044	-
	3.0	4.76	6.63	0.038	0.0370
	3.6	4.79	6.58	0.032	-
	4.0	4.82	6.55	0.029	0.0280

Table 4.4 contd...

Temp °C	Pct Mn	Pct C_{Sat}	f_s	Pct [S] $a_{MnS}=1$	Pct [S] $a_{MnS}=X_{MnS}$
	0.4	4.89	6.68	0.587	0.364
	1.0	4.91	6.63	0.237	0.190
	1.4	4.93	6.59	0.171	–
	2.0	4.95	6.54	0.120	0.107
1400	2.6	4.97	6.48	0.093	–
	3.0	5.00	6.45	0.082	0.075
	3.6	5.02	6.40	0.068	–
	4.0	5.05	6.36	0.062	0.058
	0.4	5.14	6.52	1.130	0.500
	1.0	5.16	6.47	0.462	0.309
	1.4	5.18	6.44	0.332	–
	2.0	5.20	6.39	0.233	0.189
1500	2.6	5.22	6.34	0.181	–
	3.0	5.24	6.31	0.157	0.137
	3.6	5.27	6.26	0.132	–
	4.0	5.30	6.23	0.120	0.108

4.4.4 Comparison of published data

f_s values obtained by regular solution model in Table 4.4 agree well with f_s values obtained from data of Morris[14] in Table 2.2. The calculated value of f_s around 6.85 in Table 4.4 for 1 pct Mn in the melt at 1400°C match well with the value of 6.5 from the data of Morris[14]. At 1500°C for 2.4 pct Mn in the melt, the calculated value of around 6.35 is slightly greater than the experimental value of 5.64.

4.5 Solubility of Sulphur in Fe-Mn-C-Si-S and Fe-Mn-C-P-S-Systems

The activity coefficient of sulphur increases slightly in presence of silicon and phosphorous due to the positive values of their interaction parameters and this compensates to some extent the decrease in the activity coefficient of sulphur caused by the decrease in the solubility of carbon in the melt. The results of the calculations are given in Table 4.5.

Table 4.5

Results of Calculations of Activity Coefficients and Equilibrium Sulphur Content at Different Compositions of Melt and Temperatures

Temp °C	[% Si]	[% P]	[% Mn]	[C_{sat}]	f_{Mn}	f_s	[%S]
	0	0	0.5	4.9	0.8	6.63	0.476
	2	0	0.5	4.3	0.8	7.30	0.436
	2	1	0.5	4.0	0.8	6.30	0.470
1400	0	0	2.5	4.9	0.8	6.00	0.105
	2	0	2.5	4.3	0.8	6.53	0.096
	2	1	2.5	4.0	0.8	6.12	0.102
	0	0	0.5	4.50	0.8	6.80	0.100
	2	0	0.5	3.88	0.8	7.50	0.091
1200	2	1	0.5	3.50	0.8	7.00	0.097
	0	0	2.5	4.50	0.8	6.08	0.022
	2	0	2.5	3.88	0.8	6.73	0.020
	2	1	2.5	3.50	0.8	6.23	0.022

CHAPTER V

EXPERIMENTAL DETAILS

5.1 Equipments

5.1.1 Silicon carbide furnace

A silicon carbide furnace 40 cm O.D. and 50 cm long was fabricated in the laboratory. The major parts of the furnace are schematically shown in Figure 5.1.

The inner part of the furnace is insulated by 10 cm thick hot face insulation bricks in a cylindrical fashion. Provisions are made to accomodate the furnace tube as well as silicon carbide rods inside the furnace. The outer layer of insulation consists of 5 cm thick, 85 Pct MgO, 15 Pct asbestos powder mix. This is surrounded by a metal shell which in turn is covered by a layer of asbestos cloth to reduce heat losses.

The bottom and top of the furnace are suitably insulated using 4 mm thick asbestos sheets.

The furnace tube consisted of an alumina tube 5 cm i.d. and 60 cm long with one end closed. The closed end of the alumina tube rested on a refractory base at the bottom and all the openings at top and bottom were carefully blocked by refractory pieces and cement to minimise heat losses. Alumina chips and powder were used to fill up the alumina tube upto the high temperature zone of the furnace.

ARGON

THERMOCOUPLE

REFRACTORY STOPPER

ASBESTOS SHEET

SiC ROD

Al_2O_3 TUBE

ASBESTOS
+ MgO MIX.

THERMOCOUPLE

REFRACTORY
BRICKS

METAL SHELL

ASBESTOS CLOTH

REFRACTORY

GRAPHITE
CRUCIBLE

ALLOY

Al_2O_3
CHIPS AND
POWDER
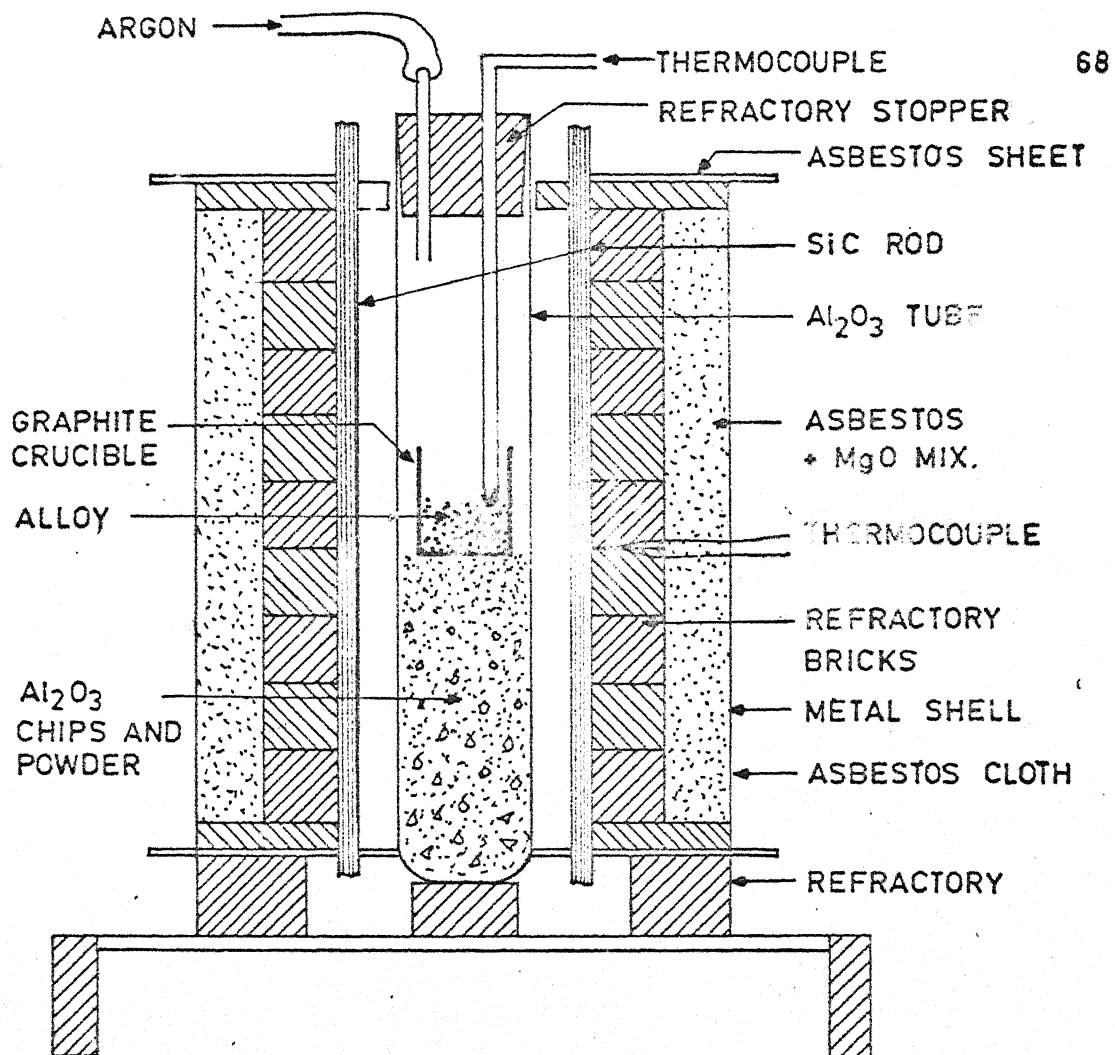
FIG. 5.1 SCHEMATIC DIAGRAM OF SILICON CARBIDE
FURNACE.

5.1.2 Transformer

Six silicon carbide rods, 1.8 cm dia, 55 cm long with 25 cm of hot zone, are connected in series by means of metallic connecting straps.

The power to the furnace is supplied by a continuously adjustable single phase, oil cooled, 40 A rating auto transformer with 220 volts input and 0-240 volts out put. The transformer was manufactured by 'Automatic Electric Private Ltd. Bombay'.

5.1.3 Temperature controller

An ON-OFF temperature controller supplied by Leeds and Northrup Co., USA was used to regulate temperature of the furnace. A 2 ohms resistance silicon carbide furnace was connected in parallel to the relay in order to supply power to the furnace at a reduced rating when the controller was in off position. The circuit diagram is schematically shown in Figure 5.2. These arrangements helped to control the temperature of the reaction tube in the furnace within the limit of $\pm 2^{\circ}C$.

5.1.4 Thermocouple

Platinum-Platinum 10 pct Rhodium thermocouple of 0.5 mm diameter, and 30 cm long was used to control the furnace temperature through the temperature controller. A separate 75 cm long Pt-Pt + 10% Rh. thermocouple of same diameter was used to measure the exact temperature of the melt. These thermocouples were periodically calibrated with melting point of pure copper and with a standard Pt-Pt + 10% Rh thermocouple, supplied by NPL, Delhi.

The thermocouple wires were protected by inserting them in twin hole thermocouple sheaths of appropriate length and 5 mm O.D. The sheaths containing the thermocouple were further inserted in a 8 mm i.d. one end closed refractory tube. The outer ends of the bigger thermocouple were connected
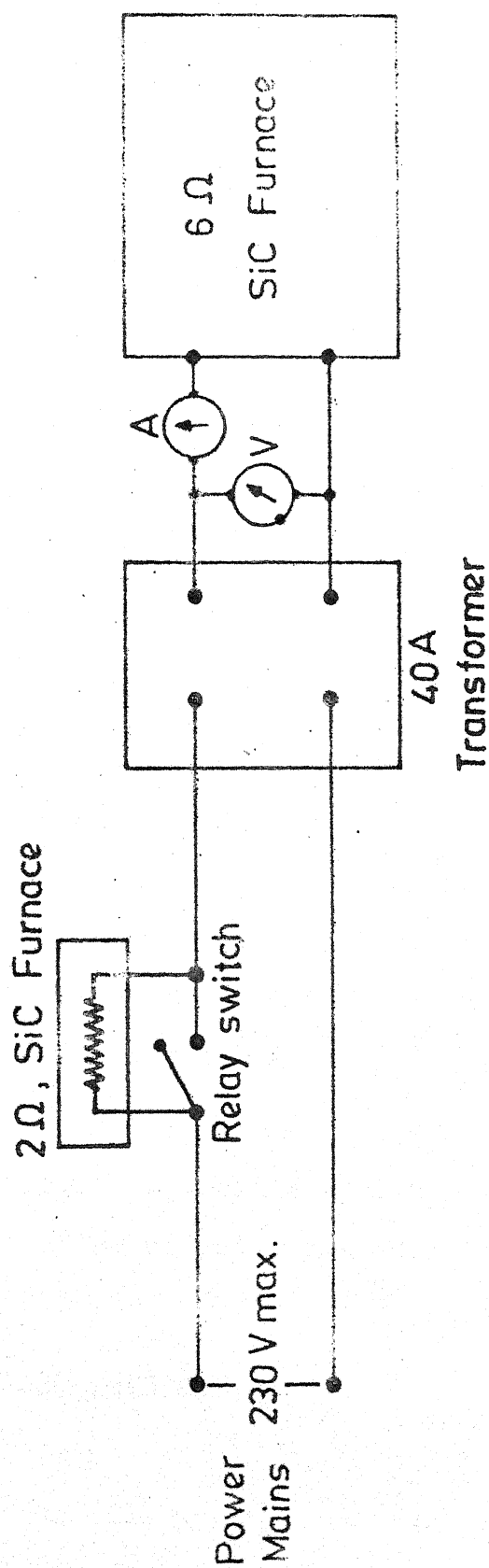
FIG. 5.2 SCHEMATIC CIRCUIT DIAGRAM FOR THE POWER SUPPLY TO THE
SILICON CARBIDE FURNACE.

to the cold junction by means of compensating wires. The cold junction consisted of 5 mm i.d. glass tubes containing mercury and it was kept inside the thermos.

A thermometer with - 10° to $100^{\circ}C$ range was used to record its temperature. The cold junction in turn was connected to the potentiometer terminals by means of copper wires, for measuring the emf generated by the thermocouple.

5.1.5 Potentiometer

The millivolt potentiometer manufactured by Leeds and Northrup, Co. U.S.A. was used to measure the emf generated by the thermocouples and this in turn could be converted to temperature by using standard tables.

5.1.6 Gas train

The neutral atmosphere of argon was maintained in most of experiments to protect the graphite crucible and the melt from the atmospheric oxidation. The argon gas was purified by passing through a calcium chloride tower to remove moisture and a copper gauze tube, maintained at $260^{\circ}-300^{\circ}C$ inside a furnace to absorb oxygen.

A calibrated capillary flow meter was used to determine the flow rate of argon being passed to the furnace through the gas train.

5.1.7 Induction furnace

The vacuum induction furnace having a capacity to melt around 500 gm of alloy, available in the crystal growth laboratory of IIT Kanpur, manufactured by Ajax, USA was used

to make the Fe-C alloys in graphite crucibles.

5.1.8 X-ray diffractometer

The X-ray diffractometer manufactured by Rich Seifert and Co., W. Germany, stationed in the ACMS Laboratory, IIT Kanpur was used for characterisation of input and output materials.

5.1.9 Atomic absorption spectro-photometer (AAS)

Model No. IL 751 , AAS manufactured by 'Instrumentation Laboratory, U.S.A., was used to analyse manganese in the sample.

5.1.10 Sulphur analysing setup

For analysing sulphur in the iron samples, the setup was made available near the experimental site. It consisted of 250 cc conical flask, B/34 glass joint, 250 cc separating funnel, glass tubes (6 mm i.d.), 100 cc measuring cylinder, and 1500 watt hot plate. The volumetric parts for titration had 50 cc burrette and 10 cc pipette. Schematic diagram of the set up is shown in Fig. 5.3.

5.2 Materials

5.2.1 Steel samples

Steel samples of 5 cm diameter and 3 cm long were collected from the open hearth bath of Durgapur Steel plant, at the end of refining, but just before addition of any ferro alloys etc.

The analyses of these samples as supplied by Durgapur Steel Plant are given in Table 5.1.

250 cc Separating Funnel

2 Cm dia.

6 mm dia.

B-34 Joint

1000 CC
Measuring
cylinder

1:1 HCl

Powdered
Sample

Ammonical
CdCl$_2$ Solution

Hot Plate
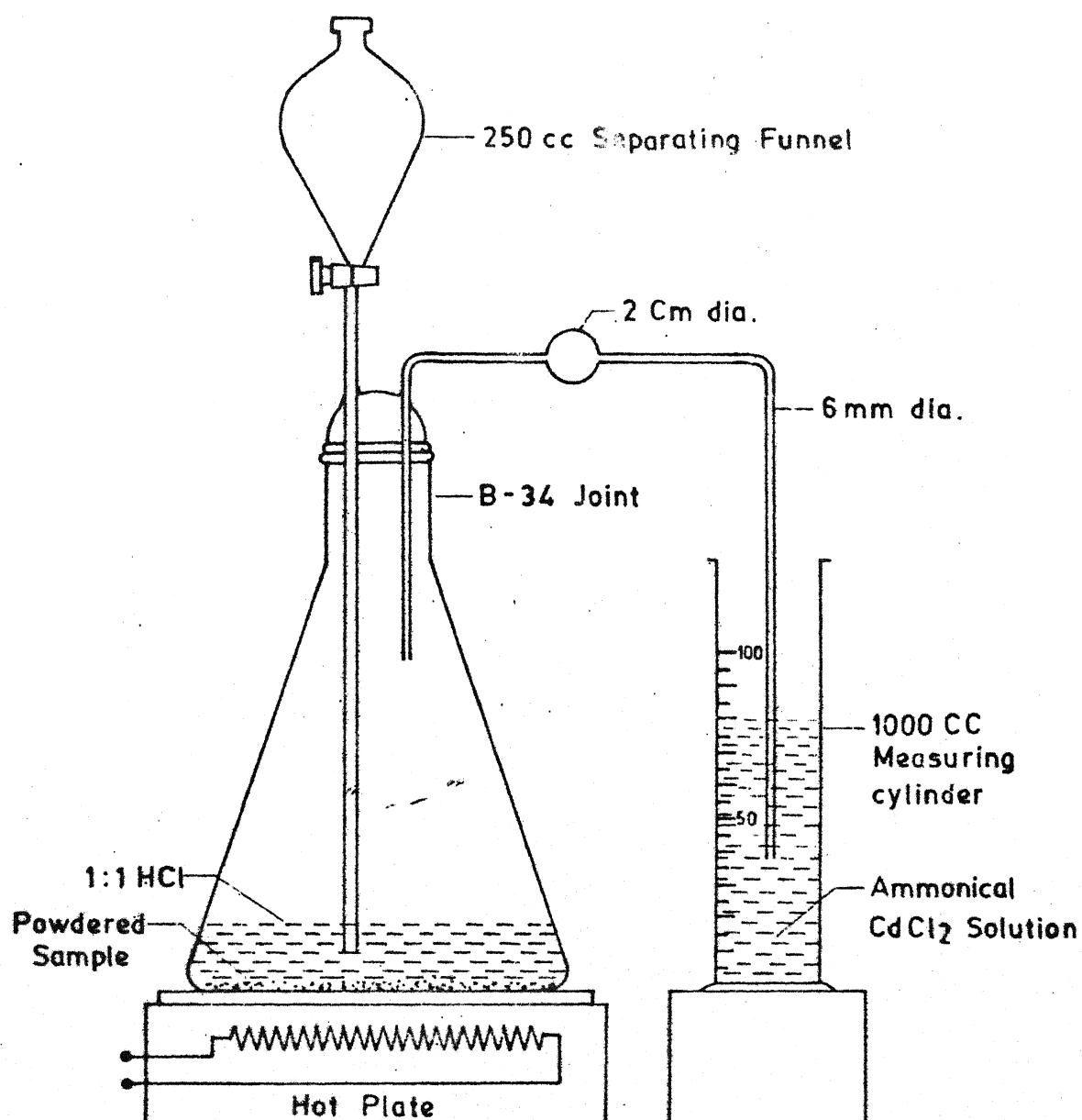
FIG. 5.3 SCHEMATIC SET UP FOR SULPHUR ANALYSIS.

Table 5.1

Chemical Analysis of Steel Samples Obtained from Durgapur Steel Plant

Sample No.	Elements , pct.				
	C	S	P	Mn	Si
1	0.12	0.048	0.020	0.05 for all samples	< 0.05 for all samples
2	0.11	0.046	0.015		
3	0.17	0.040	0.037		
4	0.14	0.038	0.015		
5	0.07	0.040	0.010		
6	0.14	0.037	0.010		
7	0.09	0.042	0.010		
8	0.20	0.040	0.025		
9	0.14	0.040	0.024		
10	0.14	0.037	0.015		
11	0.14	0.042	0.016		
12	0.12	0.036	0.020		
13	0.12	0.044	0.028		
14	0.09	0.040	0.035		
15	0.13	0.040	0.010		

5.2.2 Mn,FeS,MnS

99.9 Pct pure FeS and Mn (imported)were used for the necessary addition to the melt. In some cases FeS and MnS were obtained locally and added to melt. All raw materials were characterised using X-ray diffractometer.

5.2.3 CaO, SiO_2, Al_2O_3

99.0 Pct pure CaO, SiO_2, Al_2O_3 were used for making slags. Lime was obtained by calcination of calcite material in the laboratory at 1000 ^{o}C for one hour.

5.2.4 Graphite crucible

Graphite crucibles of 2.5 cm i.d., 7.5 cm long and 4.0 cm i.d., 10 cm long were made from 4 and 5 cm diameter locally available graphite rods, respectively.

Some crucibles were made from the broken graphite electrodes supplied by J.K. Iron and Steel,Kanpur and Singh Engineering Works, Kanpur. 5 mm holes were made at the top, sides of the crucibles to facilitate lowering of the crucible to the furnace tube using the hook of a long steel rod.

5.2.5 Sampling tube

4 to 6 mm. diameter and 1 m long silica tubes were purchased locally for drawing metal samples. One tube could be used for drawing 5 - 6 metal samples.

5.2.6 Chemical reagents

HCl, HNO_3, $CdCl_2$, Ammonia solution used for
chemical analysis of metal samples were of AR Grade, and
Sodium thiosulphate, Potassium iodide were of GR grade.
Iodine used was of LR grade.

5.2.7 Argon gas

Argon gas cylinders were available locally.

5.2.8 Standard steel sample

100 g of standard carbon steel sample, supplied by
British chemical standards No. 459/1 through their represen-
tative, Laboratory Chemical Co. Calcutta, in India, was used
to calibrate the analysing equipment.

Complete description of the standard sample as
reported by BSC is given in Table 5.2. Average values have
been obtained by analysing the sample at many places using
different methods. Manganese content varied from 0.95 to
0.99 pct. and sulphur content varied from 0.053 to 0.060 pct.

Table 5.2

Complete Analysis of the Standard Steel Sample
as Reported by the BCS

Ele-ments Pct	No. of Analysis								Average
	1	2	2	4	5	6	7	8	
C	0.514	0.521	0.518	0.524	0.534	0.522	0.530	0.521	0.523
Si	0.580	0.590	0.560	0.580	0.570	0.580	0.580	—	0.580
Mn	0.960	0.950	0.960	0.950	0.980	0.960	0.990	0.980	0.970
P	0.052	0.051	0.053	0.056	0.057	0.054	0.052	0.054	0.054
S	0.056	0.053	0.059	0.058	0.060	0.058	0.056	0.054	0.057
Al	0.026	0.027	0.028	0.028	0.030	0.026	—	—	0.028
B	0.011	0.008	0.009	0.009	0.010	0.010	0.009	—	0.010
Co	0.105	0.105	0.108	0.111	0.108	0.111	0.116	—	0.109
Nb	0.017	0.012	0.013	0.014	0.015	0.013	—	—	0.014
Pb	0.002	0.002	0.002	0.002	0.002	—	—	—	0.002
V	0.078	0.084	0.082	0.080	0.083	0.080	0.073	—	0.080
Zr	0.072	0.070	0.069	0.075	0.073	—	—	—	0.072
Sb	0.006	0.006	0.006	0.007	0.006	0.006	0.006	—	0.006

5.3 Experimental Procedure

5.3.1 Calibration of thermocouple

The thermocouple (Pt-Pt + 10% Rh) was calibrated against melting point of pure copper. 99.9 pct. pure copper was taken in a graphite crucible and melted in the silicon carbide furnace under argon atmosphere. The arrest point was noted by recording temperature of the melt as function of time during cooling.

5.3.2 Calibration of capillary flowmeter

The capillary flow meter was calibrated by noting the time of travel of the soap bubble in a glass tube of known volume, when argon gas was being passed, and by measuring at the same time the difference in heights in the two fluid columns of the flow meter.

5.3.3 Making iron-carbon alloys

The steel samples from Durgapur steel plant were machined to 35 mm dia. cylinders, which were then washed with acetone.

About 400 g of the prepared samples were put in graphite crucibles of 40 mm i.d., 10 cm long. The crucible with the steel sample was placed in the vacuum induction furnace. Steel samples melted in an hour or so and picked up carbon from the graphite crucible. The temperature of the furnace as recorded by the optical pyrometer was around 1550-1600 ^{o}C.

On cooling, the crucible was removed from the furnace and the alloy was recovered by breaking the crucible. It was then broken in to small pieces (10 mm size or less) by hammering. The sized Fe-C alloy was used subsequently for melting in the SiC furnace for investigations as described later.

5.3.4 Making slags

Lime, alumina and silica materials were properly weighed and mixed to obtain the CaO/SiO_2 ratio 1, 1.5 and 2, with Al_2O_3 percentage kept at 20 pct in the final slag.

The mixture was kept in a graphite crucible, 2.5 cm i.d. 7.5 cm long and placed inside the silicon carbide furnace under argon atmosphere at $1400^{\circ}C$. After 15-20 minutes, the constituents in the crucible became nearly molten. The molten slag was stirred by a graphite rod for half an hour. The cruicible was taken out of the furnace and allowed to cool. The solidified slag was obtained by breaking the cruicibles.

5.3.5 Mn-S equilibrium in Fe-C alloys

The graphite crucible with 70-100 g of the Fe-C alloy and other additions such as Mn, FeS , MnS etc. was lowered into the reaction tube, which was being purged by argon before hand. The argon supply tube (6mm i.d. Al_2O_3 tube) had to be taken out and reinserted into the reaction tube during the process of lowering the graphite cruc i ble.

Continuous stirring of the melt was provided manually using a graphite rod. Sufficient time was allowed to reach equilibrium. The exact temperature of the melt was determined by placing the thermocouple just above the melt. Normally the temperature of melt differed from the temperature recorded by the other thermocouple by $30^{o}C$ or so.

The alloy samples were sucked by dipping one end of the silica tube in the melt and using an aspirator at the other end. At a time 10-15 gm. of samples could be collected. The sample tube was repeatedly purged with argon to minimise oxidation of melt by the entrapped air during sampling.

5.3.6 Slag metal equilibrium

The graphite crucible was loaded with desired quantity of iron-carbon alloy and the premelted slag. The temperature was kept constant at $1400^{o}C$ in such experiments to ensure that slag remained in the molten form. The alloy sample was sucked in similar fashion as described previously.

In some cases the crucible was taken out of the furnace after the experiment and samples were taken from the solidified mass after breaking the crucible.

5.3.7 Chemical analysis of samples

The samples to be analysed were first powdered to 100 mesh size in a pestle, mortar.

5.3.7.1 Manganese

For analysis of Manganese by Atomic Absorption spectrophotometer the following steps were followed.

1) Preparation of solutions

0.1 gm of Mn (99.9 Pct pure), standard steel sample and unknown samples were weighed separately and dissolved in 10 ml of 1:3 HNO_3 and diluted to 100 ml after filtering. The stock solution prepared above were further diluted to the desired concentration. Solution of pure Mn were diluted to 0.2 ppm.

2) Procedure

The following instrumental condition for Mn analysis were fixed.

Hollow cathode lamp   = Mn

Wave length   = 279.5 nm

Flame = Air - acetylene

Absorbance of the solutions of known concentration is measured to obtain the linear plot between absorbance and concentration. From this plot and the measured absorbance of the unknown solution, its manganese concentration can be determined.

5.3.7.2 Silicon

Some samples were analysed for silicon by gravimetric method in the Analytical Laboratory of Metallurgical Engineering Department, IIT Kanpur.

5.3.7.3 Sulphur

Sulphur was analysed by evolution technique in the laboratory.

The following procedure was followed:

(1)   The set up was tested of any leakage of the gas. This was done by pressurising the vessel with argon and then noting any pressure drop in the line when the supply of argon was cut off.

(2)   Around 5 gm of the powdered sample was transferred carefully to the conical flask. The glass joint was placed on the proper position. The exit end of the glass tube was dipping in an ammonical cadmium chloride solution of 1 gm $CdCl_2$ in 60 ml of distilled water. 80 ml of 1:1 HCl was poured into the flask from the separating funnel. The hot plate was switched on. The heat was regulated by operating the regulator of the hot plate. Heat supply was increased towards the end of the analysis in order to flush out the sulphur gas completely from the system by the vapours of H_2O.

The sulphur in the alloy reacted with HCl to form H_2S gas, which was absorbed by the ammonical $CdCl_2$ solution to form precipitate of cadmium sulphide. When it was confirmed that the alloy sample dissolved completely and H_2S gas was flushed out of the flask the absorbing solution was cooled in an ice bath. The ice cold solution was acidified with 20 ml of concentrated HCl. To the acidified solution 10 cc of N/10 iodine solution was added and titrated against N/10 $Na_2S_2O_3$ solution. 10 cc of N/10 iodine solution was also titrated against N/10 $Na_2S_2O_3$ solution in each case. The difference in two values of N/10 $Na_2S_2O_3$ amounts is the equivalent amount of $Na_2S_2O_3$ solution consumed for sulphur in the sample.

The pct sulphur in the sample was calculated as follows:

$$\% S = \frac{0.16 \, Y}{X}$$

where 'Y' is the amount of $N/10$ $Na_2S_2O_3$ solution consumed for sulphur and X is the weight of sample in grams.

5.3.8 Characterisation of phases by x-ray diffractometer

Prepared sample of less than 0.15 mm size was used for characterisation of phases of the materials.

The instrumental conditions were as follows:

2θ angle was varied from 15° to 100°

The scanning speed was kept at 3° per min.

Cr-radition with $\lambda = 2.291 \, \overset{\circ}{A}$ was used. From the peaks at different 2θ values, the d values are calculated by the following relation;

$$\lambda = 2 \, d \, \sin \theta.$$

CHAPTER   VI

RESULTS

6.1   Fe-C-Mn-S System

The desired quantity of iron carbon master alloy, manganese and sulphur in the form of FeS were added in the graphite crucible so as to give 100 gm of the liquid alloy on melting. In some cases, when sulphur in the form of MnS or FeS + MnS was also added to the graphite crucible, about 75 g of Fe-C alloy was added to it. Table 6.1 summarises the quantity of materials added before or during melting.

6.1.1   Cooling and heating of melt at almost constant Mn level

The results of chemical analysis i.e. S and Mn content of the samples drawn at different temperatures from the melt in each case are also given in Table 6.1. The samples at about 1300°C were taken both during cooling and heating cycles in all cases to check whether equilibrium is reached or not.

In each case the melt was allowed to remain at 1300°C for one hour. In one experiment i.e. H_6 the melt was allowed to remain at 1300°C for another hour before drawing any additional sample. There was good agreement between the two values at the same temperature and this also signified the attainment of equilibrium in one hour at a particular temperature.

Table 6.1

Experimental [Mn] pct and [S] pct in Iron-Carbon Alloys at Temperatures 1200°-1400°C

Heat No.	Time Hours	Input Materials Quantity, gms				Temp. °C	Holding time hour	Sample No.	Mn pct	S pct
		Fe-C Alloy	Mn	FeS	MnS					
1	2	3	4	5	6	7	8	9	10	11
H_1	0.0	97.8	0.0	2.2	0.0	1360	1	H_1-S_1	N.A.	0.770
	1.0	-	0.0	-	0.0	1260	1	H_1-S_2	N.A.	0.750
H_2	0.0	98.2	1.1	0.825	0.0	1400	1	H_2-S_1	0.84	0.148
	1.5	-	-	-	-	1300	1	H_2-S_2	0.84	0.075
	3.0	-	-	-	-	1200	1	H_2-S_3	0.84	0.050
	4.5	-	-	-	-	1300	1	H_2-S_4	0.84	0.070
H_3	0.0	92.8	1.18	1.04	0.0	1360	1	H_3-S_1	0.91	0.116
	1.5	-	-	-	-	1290	1	H_3-S_2	0.91	0.087
	3.0	-	-	-	-	1200	1	H_3-S_3	0.90	0.047
	4.5	-	-	-	-	1290	1	H_3-S_4	0.90	0.084
H_4	0.0	96.5	2.2	1.26	0.0	1350	1	H_4-S_1	1.50	0.056
	1.5	-	-	-	-	1290	1	H_4-S_2	1.50	0.042
	3.0	-	-	-	-	1210	1	H_4-S_3	1.50	0.028
	4.5	-	-	-	-	1290	1	H_4-S_4	1.50	0.040

Table 6.1 contd...

1	2	3	4	5	6	7	8	9	10	11
H5	0.0	94.0	3.1	1.13	0.0	1360	1	H5-S1	2.6	0.057
	1.5	–	–	–	–	1290	1	H5-S2	2.6	0.032
	3.0	–	–	–	–	1200	1	H5-S3	2.6	0.020
	4.5	–	–	–	–	1290	1	H5-S4	2.6	0.030
H6	0.0	100.4	4.42	1.18	0.0	1360	1	H6-S1	3.6	0.031
	1.5	–	–	–	–	1290	1	H6-S2	3.6	0.026
	2.5	–	–	–	–	1290	1	H6-S3	3.6	0.025
	4.0	–	–	–	–	1210	1	H6-S4	3.6	0.016
	5.5	–	–	–	–	1290	1	H6-S5	3.6	0.024
H7*	0.0	95.0	2.2	1.15	0.0	1400	1	H7-S1	1.6	0.070
	1.5	–	–	–	–	1300	1	H7-S2	1.6	0.045
	3.0	–	–	–	–	1210	1	H7-S3	1.6	0.031
	4.5	–	–	–	–	1300	1	H7-S4	1.6	0.042
	5.5	–	–	–	–	1300	1	H7-S5	1.6	0.044
H8	0.0	70.0	1.05	0.00	7.0**	1400	4	H8-S1	1.1	0.140
	4.5	–	–	–	–	1300	2	H8-S2	1.0	0.084
	7.0	–	–	–	–	1200	2	H8-S3	1.0	0.044
	9.5	–	–	–	–	1300	4	H8-S4	1.0	0.082
H9	0.0	50.0	2.00	5.00	0.0	1300	1	H9-S1	<.1	1.08

*   2.2 gms FeSi added at zero hour

** local grade

Additional experiments were carried out to study the approach to the equilibrium during cooling of the melt without any stirring as to simulate the conditions in the ladle during the transit from the blast furnace section to the steel making section. Samples were drawn during cooling as soon as the temperatures of about $1300^{o}C$ and $1200^{o}C$ were recorded. The values are summarised in Table 6.2.

In one experiment i.e. H_9 enough Mn and FeS was added with the Fe-C alloy. After melting and holding for one hour the graphite crucible containing the melt was taken out and allowed to cool in air. It was then broken to collect the metal and slag samples for chemical analysis and X-ray diffraction study.

6.1.2 Stepwise additions of manganese at constant temperature

In some experiments Mn content of the melt was increased by stepwise addition of Mn at a constant temperature. The results of these experiments are summarised in Table 6.3.

6.2 Slag Metal Equilibrium Studies

The desulphurisation capacity of the oxide slag S' was studied at different manganese levels in the metal at $1400^{o}C$. Mn was added to the melt in steps and samples were drawn through silica tube after allowing the melt to reach equilibrium in 4 hours with constant stirring of the bath. The details of experiments and the results of chemical analysis are given in Table 6.4.

Table 6.2

Results of Experiments of the Cooling the Melt from $1400^{o}C$

Heat No.	Sample No.	Input materials, gms			Time Mins.	Temp. ^{o}C	Metal Analysis pct	
		Fe-C Alloy	Mn	FeS			Mn	S
	$H_{10}-S_1$	80	1.9	0.9	0	1390	1.7	0.083
H_{10}	$H_{10}-S_2$	–	–	–	10	1275	1.7	0.048
	$H_{10}-S_3$	–	–	–	15	1220	1.7	0.044
	$H_{11}-S_1$	80	1.9	0.9	0	1388	1.6	0.065
H_{11}	$H_{11}-S_2$	–	–	–	44	1300	1.6	0.038
	$H_{11}-S_3$	–	–	–	84	1220	1.6	0.031

Table 6.3

Experimental Results of Stepwise Addition of Mn at 1325° and 1400°C

Heat No.	Time Hour	Input Materials : gms				Temp. °C	Holding Time Hour	Sample No.	Sample Wt. gms	Mn pct	S pct
		Fe-C Alloy	Mn	FeS	MnS						
H12	0	89.4	4.0	6.875*	0.0	1325	2	H12-S1	15	1.27	0.084
	2	—	1.0	—	—	1325	1	H12-S2	15	2.35	0.047
	3	—	1.0	—	—	1325	1	H12-S3	10	3.26	0.036
H13	0	70.0	0.00	7.000**	0.0	1400	4	H13-S1	10	0.371	0.347
	4	—	0.90	—	—	1400	4	H13-S2	10	1.320	0.110
	8	—	0.54	—	—	1400	2	H13-S3	10	2.160	0.069
	10	—	0.42	—	—	1400	2	H13-S4	10	3.140	0.057
H14	0	70.0	0.00	3.5**	3.5**	1400	4	H14-S1	10	0.200	0.680
	4	—	1.00	—	—	1400	4	H14-S2	10	0.600	0.230
	8	—	0.55	—	—	1400	2	H14-S3	10	1.320	0.095
	10	—	0.42	—	—	1400	2	H14-S4	20	2.160	0.064

* Imported grade

** Local grade

Table 6.4

Experimental Results of Slag-Metal Equilibrium at 1400°C

Slag composition:

Slag	% CaO	% SiC$_2$	% Al$_2$O$_3$
A	40	40	20
B	48	32	20
C	53.4	26.6	20
D	100	0	0

Heat No.	Time Hour	Input Materials gms				Holding time hour	Sample No.	Mn pct	S pct	Si pct
		Fe-O Alloy	FeS	Mn	Slag Quantity					
1	2	3	4	5	6	7	8	9	10	11
H$_{15}$	0	75.0	1.00	0.00	A-4	2	H$_{15}$-S$_1$	-	0.256	-
	2	-	-	-	-	2	H$_{15}$-S$_2$	-	0.221	-
H$_{16}$	0	80.0	1.00	0.00	A-8	2	H$_{16}$-S$_1$	-	0.152	-
	2	-	-	-	-	2	H$_{16}$-S$_2$	-	0.144	-
H$_{17}$	0	78.8	0.90	1.20	A-4	2	H$_{17}$-S$_1$	1.20	0.108	-
	2	-	-	-	-	2	H$_{17}$-S$_2$	1.11	0.096	-
H$_{18}$	0	78.0	0.90	1.20	A-8	2	H$_{18}$-S$_1$	1.15	0.070	-
	2	-	-	-	-	2	H$_{18}$-S$_2$	1.14	0.000	-

Contd......

Table 6.4 contd....

1	2	3	4	5	6	7	8	9	10	11
H_{19}	0	78.0	0.87	2.0	A-4	2	$H_{19}-S_1$	2.07	0.073	–
	2	–	–	–	–	2	$H_{19}-S_2$	2.06	0.064	–
H_{20}	0	73.0	0.90	2.10	A-8	2	$H_{20}-S_1$	2.20	0.054	–
	2	–	–	–	–	2	$H_{20}-S_2$	2.12	0.048	
H_{21}	0	75.0	0.83	0.00	A-15	4	$H_{21}-S_1$	–	0.116	–
	4	–	–	1.00	–	4	$H_{21}-S_2$	1.25	0.060	–
	8	–	–	0.50	–	4	$H_{21}-S_3$	2.00	0.040	–
*H_{22}	0	75.0	0.834	0.00	A-15	4	$H_{22}-S_1$	–	0.096	–
	4	–	–	0.90	–	4	$H_{22}-S_2$	1.00	0.070	–
	8	–	–	0.60	–	4	$H_{22}-S_3$	2.08	0.040	0.58
**H_{23}	0	76.0	0.830	0.00	B-7.08	4	$H_{23}-S_1$	–	0.076	–
	4	–	–	0.98	–	4	$H_{23}-S_2$	1.09	0.043	–
	8	–	–	0.60	–	4	$H_{23}-S_3$	1.54	0.035	–
H_{24}	0	75.0	0.820	0.00	B-15	4	$H_{24}-S_1$	–	0.046	–
	4	–	–	1.00	–	4	$H_{24}-S_2$	1.27	0.028	–
	8	–	–	0.50	–	4	$H_{24}-S_3$	2.15	0.016	0.31

Contd......

Table 6.4 contd...

1	2	3	4	5	6	7	8	9	10	11
***H25	0	76.0	0.83	0.00	0-7.9	4	H25-S1	-	0.060	-
	4	-	-	1.00	-	4	H25-S2	1.23	0.012	-
	8	-	*	0.55	-	4	H25-S3	2.32	0.006	0.25
H26	0	75.0	0.83	0.00	0-15	4	H26-S1	-	0.012	-
	4	-	-	0.98	-	4	H26-S2	1.31	0.009	-
	8	-	*	0.60	-	4	H26-S3	2.20	0.006	-
H27	0	76.0	0.9	0.00	0-7.7	4	H27-S1	-	0.010	-
	4	-	-	1.00	-	4	H27-S2	1.29	0.008	-
	8	-	-	0.60	-	4	H27-S3	2.22	0.007	-

*   1.61 pct Mn in final slag

**   0.76 pct Mn in final slag

***   0.54 pct Mn in final slag

Table 6.5

Experimental Results to Establish Slag-Metal Equilibration Time at 1400°C

Slag	% CaO	% SiO$_2$	% Al$_2$O$_3$
A	40	40	20
C	53.4	26.6	20

Heat No.	Time Hour	Input Materials in gms				Holding time hour	Sample No.	Mn pct	S pct
		Fe-C Alloy	FeS	Mn	Slag-Quantity				
H$_{28}$	0	75.0	0.83	1.21	A-15	4	H$_{28}$-S$_1$	1.29	0.068
	4	—	—	—	—	4	H$_{28}$-S$_2$	1.20	0.067
	8	—	—	—	—	4	H$_{28}$-S$_3$	1.18	0.068
H$_{29}$	0	75.0	0.82	0.00	C-7.5	4	H$_{29}$-S$_1$	—	0.051
	4	—	—	—	—	4	H$_{29}$-S$_2$	—	0.049
	8	—	—	—	—	4	H$_{29}$-S$_3$	—	0.050

Table 6.6

Experimental Results of Slag Metal Equilibrium at 1400°C

| Heat No. | Sample No. | Input materials in gms | | | | Compound | | | Holding Time Hour | Metal Analysis pct | |
		Fe-C Alloy	FeS	Mn	Slag	CaO %	SiO %	Al_2O_3 %		Mn	S
H30	H30-S1	30	0.33	–	6	40.0	40.0	20	6	–	0.096
H31	H31-S1	30	0.33	0.210	3	40.0	40.0	20	6	0.45	0.135
H32	H32-S1	30	0.33	0.210	6	40.0	40.0	20	6	0.48	0.096
H33	H33-S1	30	0.33	0.434	6	40.0	40.0	20	6	0.99	0.071
H34	H34-S1	30	0.33	–	6	48.0	32.0	20	6	–	0.043
H35	H35-S1	30	0.33	0.210	6	48.0	32.0	20	6	0.47	0.041
H36	H36-S1	30	0.33	0.434	6	48.0	32.0	20	6	0.92	0.030
H37	H37-S1	30	0.33	0.210	3	48.0	32.0	20	6	0.55	0.075
H38	H38-S1	30	0.33	–	6	53.4	26.6	20	6	–	0.020
H39	H39-S1	30	0.33	0.210	6	53.4	26.6	20	6	0.53	0.016
H40	H40-S1	30	0.33	0.434	6	53.4	26.6	20	6	1.08	0.011
H41	H41-S1	30	0.33	0.210	3	53.4	26.6	20	6	0.47	0.017

Table 6.7

Results of Rechecked Sulphur Determinations on Metal Samples

Sample No.	Pct Sulphur	
	1st Analysis	2nd Analysis
H_3-S_1	0.116	0.112
H_4-S_4	0.040	0.039
H_5-S_4	0.029	0.030
$H_{17}-S_2$	0.096	0.116
$H_{21}-S_3$	0.040	0.042
$H_{24}-S_3$	0.016	0.014

Table 6.8

Analysis of Standard Steel Sample in the Laboratory

Sl.No.	Percentage of S Reported, Average Value	Percentage of S As Analysed in the Laboratory
1	0.057	0.054
2		0.051
3		0.048
4		0.049
5		0.052
6		0.053
7		0.048
8		0.051
	Average	0.051

6.4 X-Ray Characterisation of Materials

X-ray diffraction pattern to characterise various materials such as steel samples from Durgapur, Manganes (imported) iron sulphide (imported), iron sulphide (local), manganese sulphide(local),prepared iron-carbon master alloy in the laboratory by induction melting, prepared manganese sulphide in laboratory by the reaction between stochiometric amounts of molten iron sulphide and manganese in graphite crucible at around $1365^{o}C$, collected slag samples of some heats are given in Figures 6.1 to 6.4.
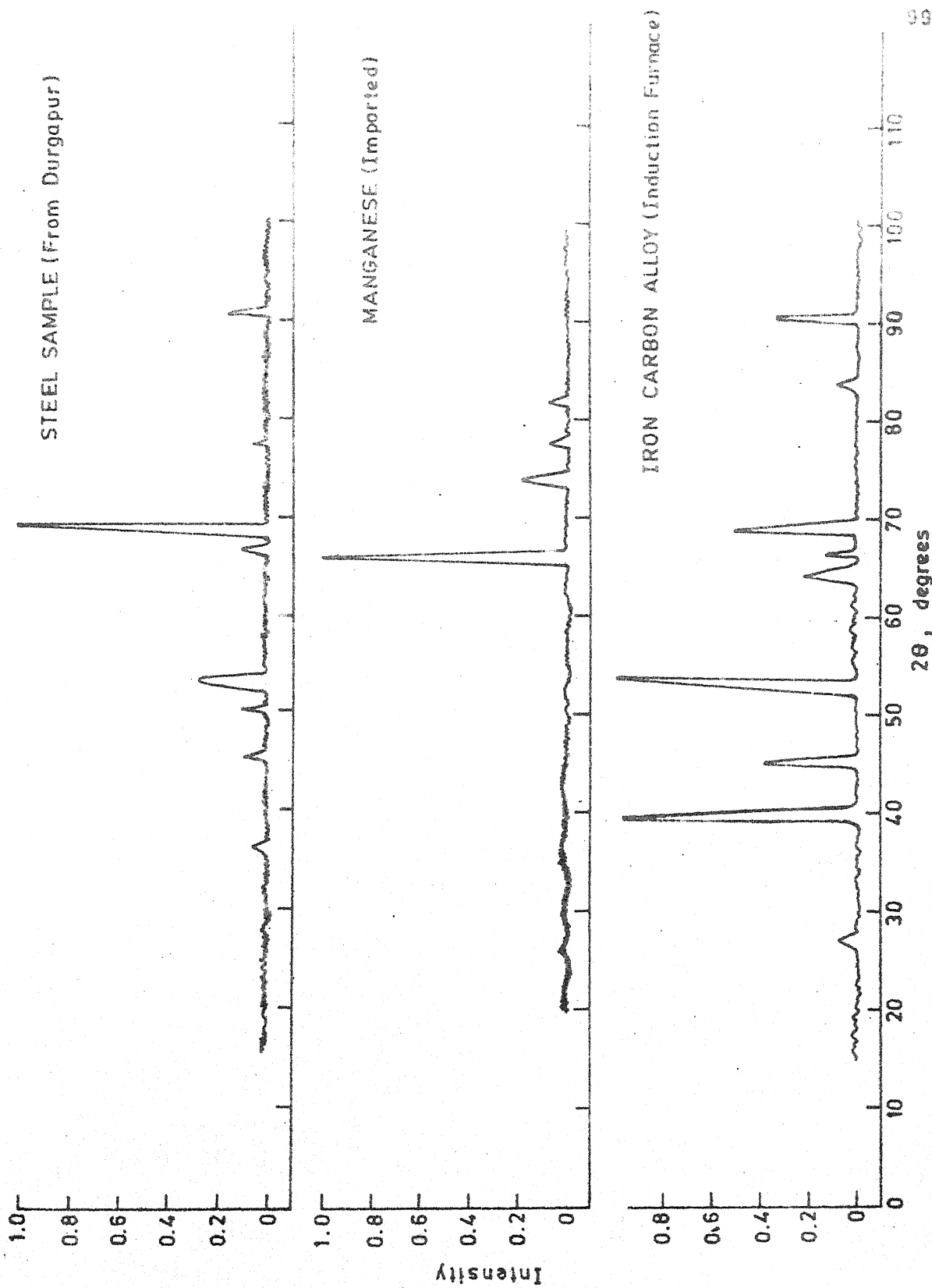
FIG. 6.1 X-RAY DIFFRACTION PLOTS FOR IRON, MANGANESE AND IRON-CARBON ALLOY
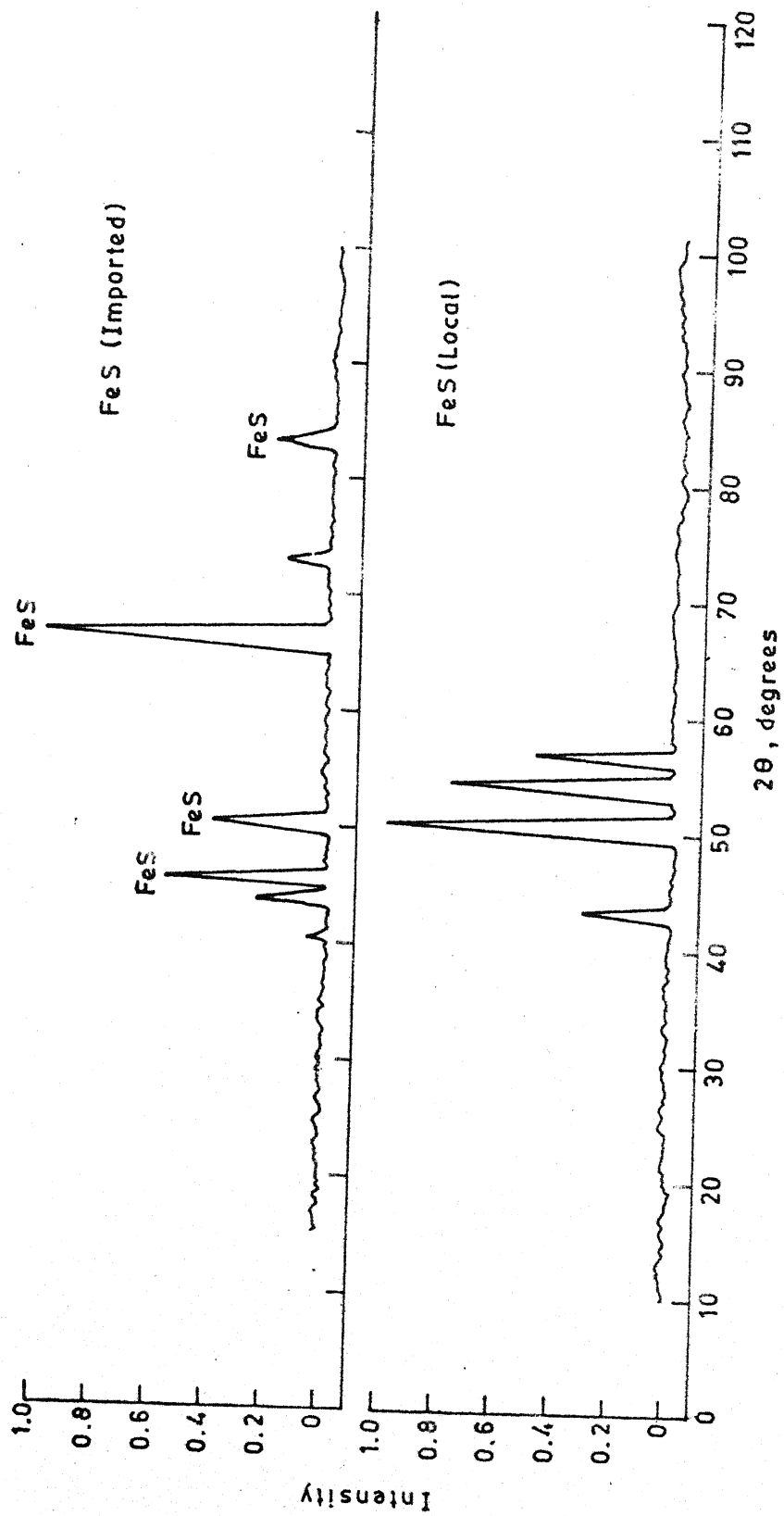
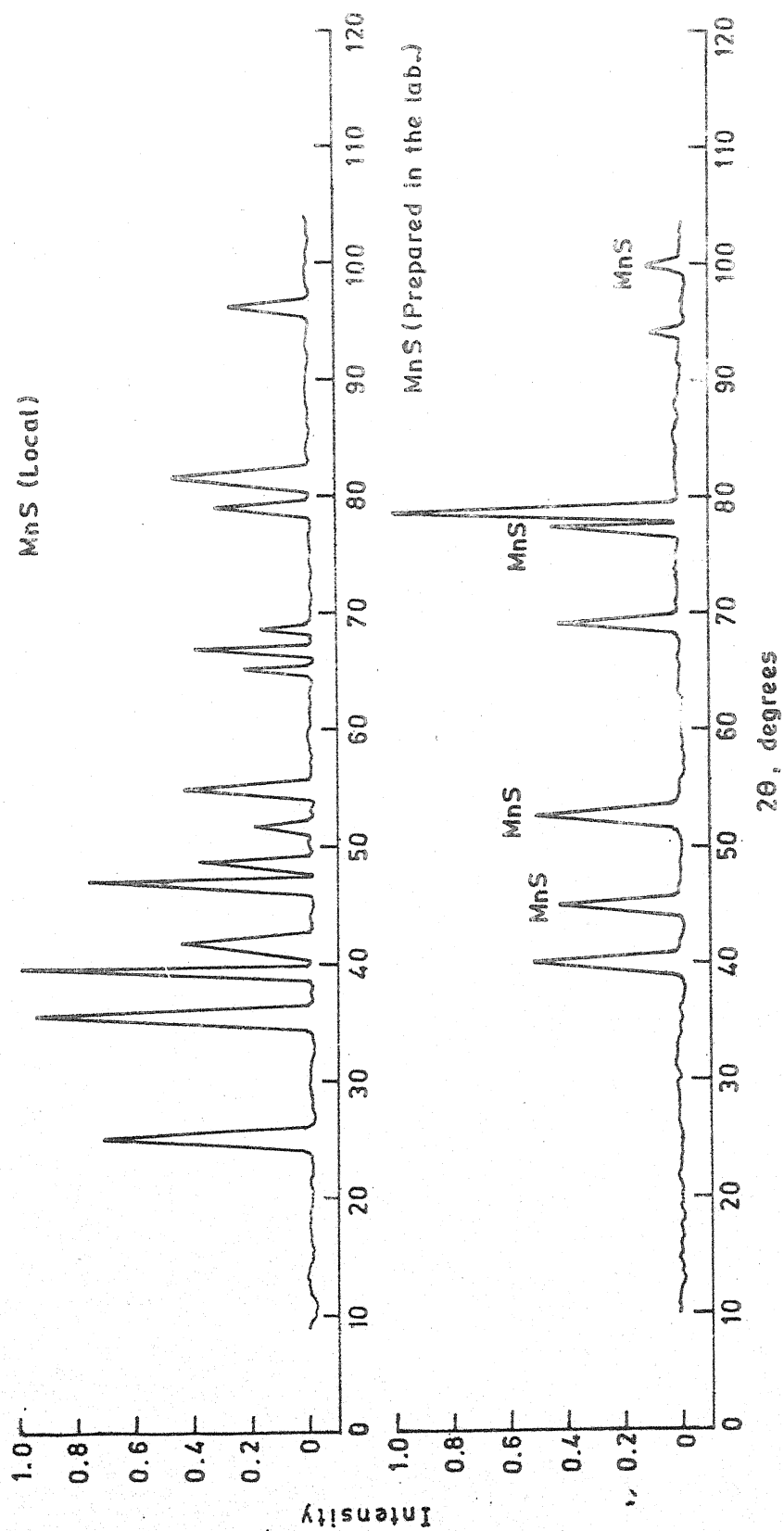FIG. 6.2 X-RAY DIFFRACTION PLOTS FOR IRON SULPHIDE IMPORTED AND LOCAL.

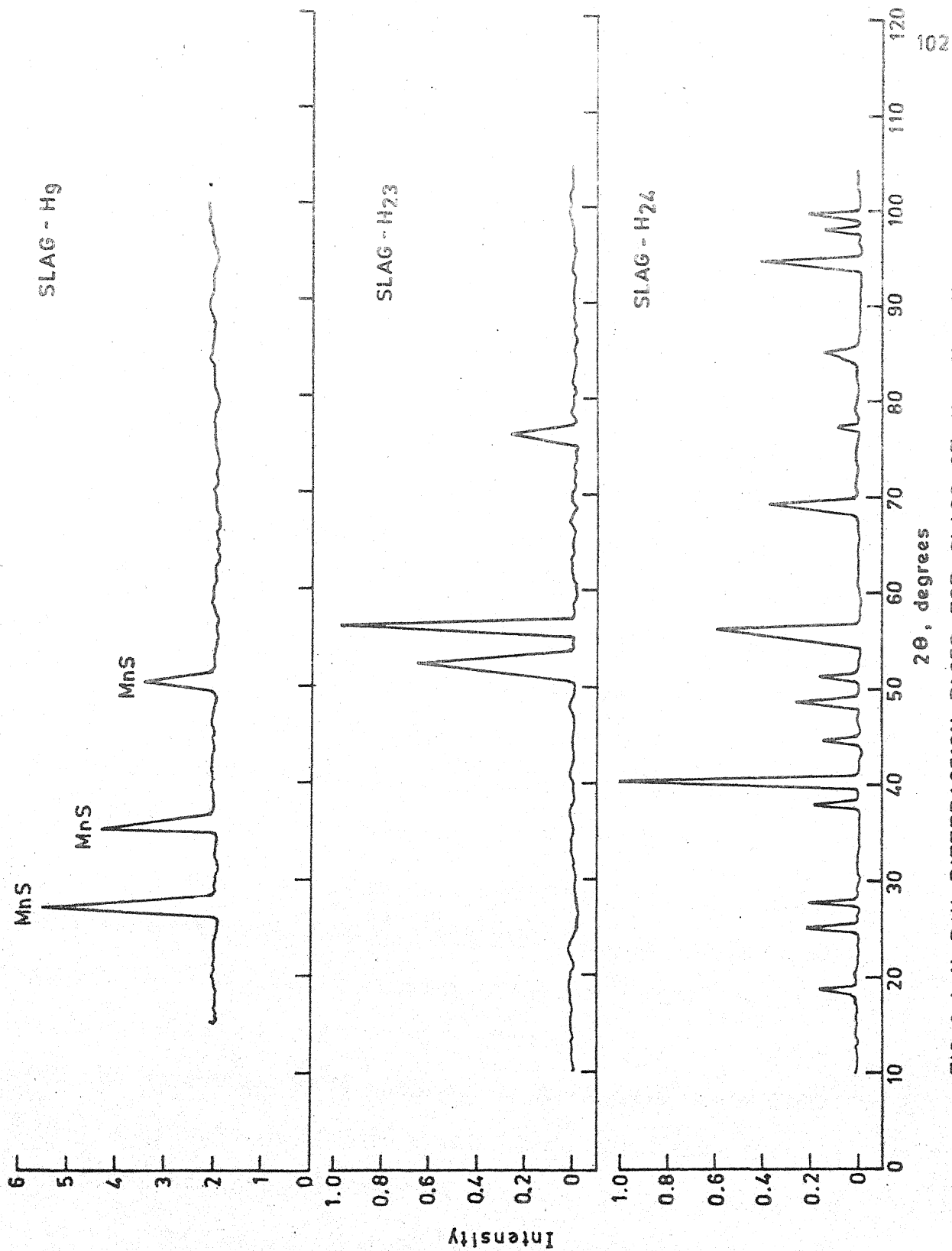FIG. 6.3 X-RAY DIFFRACTION PLOTS FOR MnS LOCAL AND PREPARED IN THE LAB

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FIG. 6.4 X-RAY DIFFERACTION PLOTS FOR SLAGS OF H9, H23, H24.

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CHAPTER VII

DISCUSSION

7.1 Manganese Sulphur Equilibrium

7.1.1 Reliability of data

Determination of the manganese or sulphur contents in the samples of the iron alloys as reported in Chapter 6 can be believed to be quite accurate because of the good agreement obtained between the reported analysis and the actual analysis of the standard steel samples, and also because of the agreement reached between the two values of the same sample in a few cases. For these melts quantity of the slag formed may be around one percent or so and this did not pose any problem in sucking the metal sample from the bottom of the crucible. From the theoretical analysis given in Chapter 4, it is possible to calculate the equilibrium sulphur level in the melt at a particular temperature and manganese content of the metal. The experimental values of the sulphur analyses are compared with the calculated values in Figure 7.1.

Agreement is quite good especially for those samples which were taken at 1200°C. Similar analysis was done to compare the experimental values of Morris[14] with the calculated values as shown in Figure 7.2. Morris's[14] results agreed with the theoretical calculations both at 1200°C and 1400°C. At higher temperatures of 1350°C and 1400°C, the experimental results of the present study are lower than the calculated values. This discrepancy may be attributed due to any of the
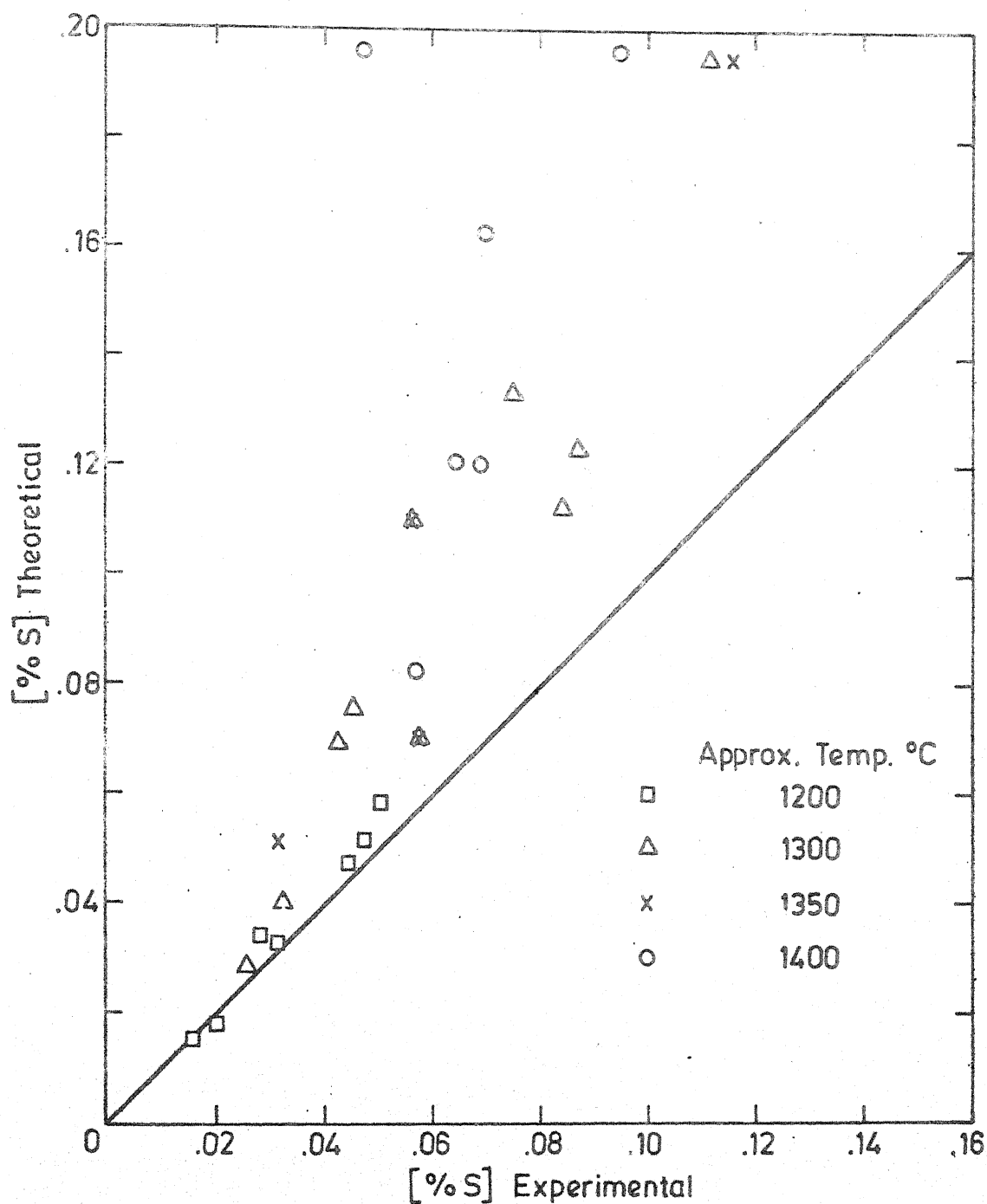
FIG. 7.1 COMPARISON OF EXPERIMENTALLY DETERMINED SULPHUR
VALUES WITH THEORETICALLY CALCULATED SULPHUR
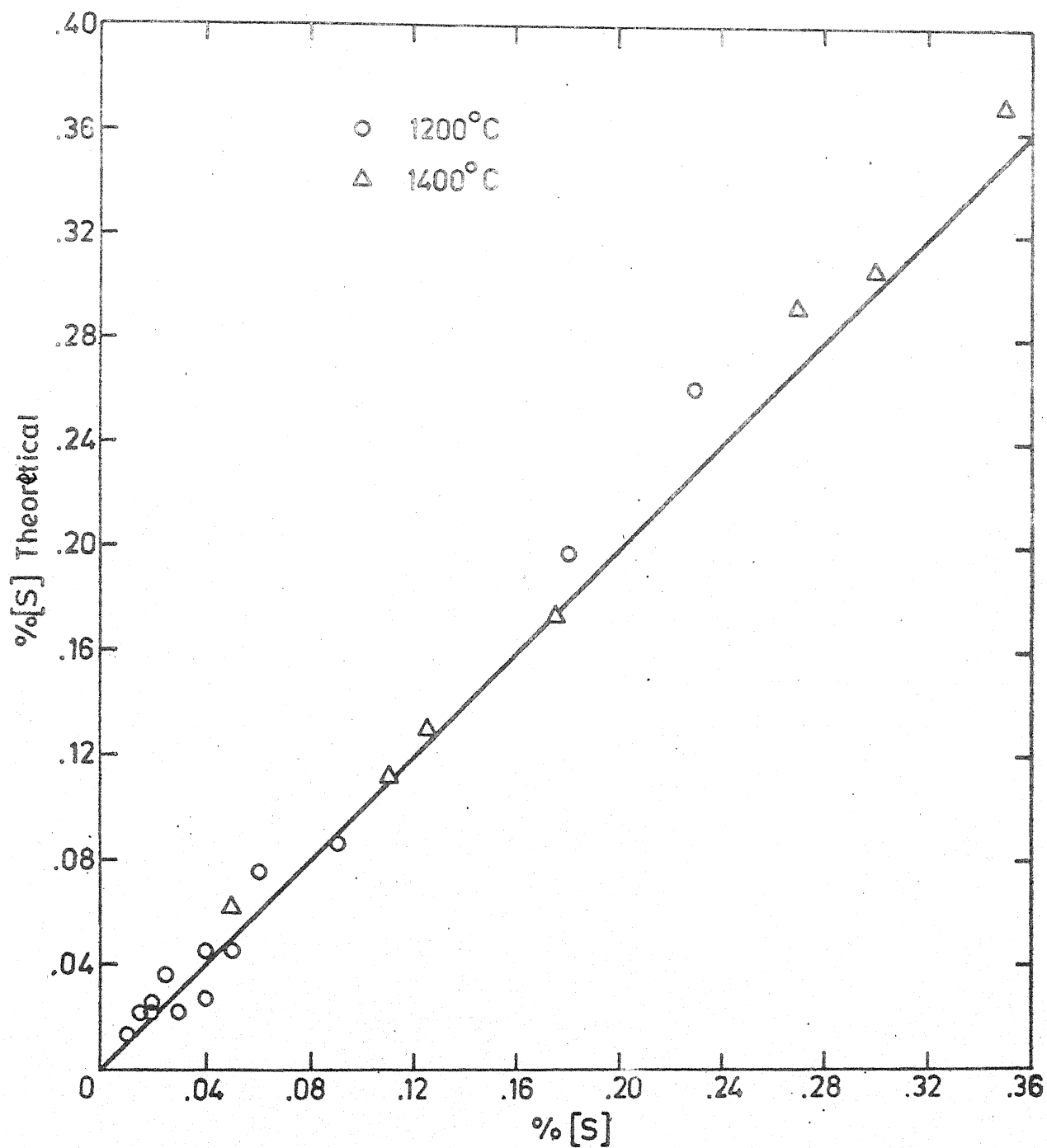VALUES FROM THERMODYNAMIC DATA.

FIG. 7.2 COMPARISON OF MORRIS'S DATA WITH THEORETICALLY
CALCULATED SULPHUR VALUE

following;

(1)   Experimental errors in estimating temperature, manganese and sulphur levels of the melt.

(2)   Formation of MnO, FeO or SiO_2 in the slag so as to lower the activity of MnS in the slag at higher temperatures.

(3)   Formation of FeS in the slag especially at higher sulphur levels of the melt as to lower the activity of MnS in the slag.

Experimental errors in estimating temperature, manganese or sulphur can not explain the discrepany because enough care was taken to control them. Thermocouples were properly and periodically calibrated and the tip of the thermocouple lied very close to the melt. The argon tube was positioned at 20 cm above the melt and it cannot account for any temperature gradient within the melt.

Any FeO or MnO formed due to oxidation of metal by oxygen in the argon gas will react immediately with graphite crucible as per the following reaction;

$$(FeO) + C(gr) = Fe + CO \qquad (7.1)$$

$$(MnO) + C(gr) = [Mn] + CO \qquad (2.31)$$
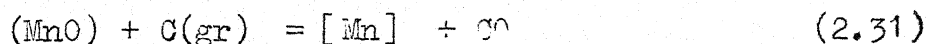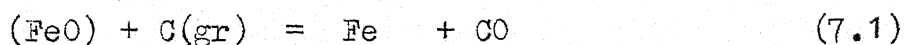
$$K_{2.31} = \frac{f_{Mn}\,[\,Wt\%\ Mn\,]}{a_{MnO}\ a_C}\ p_{CO} \qquad (7.2)$$

$$\log K_{2.31} = -\frac{15090}{T} + 10.90 \qquad (7.3)$$

For carbon saturated iron $a_C = 1$ and $f_{Mn} = 0.8$ and taking $p_{CO} = 1$ atm., from equation (7.2) and (7.3), a_{MnO} value at $1300^\circ C$ is 0.039 for one percent manganese in the melt. Since reaction is occuring at the slag metal interface p_{CO} can be taken as one atm. Otherwise its value will be lowered as to decrease a_{MnO} further. Thus thermodynamic calculations show that a_{MnO} in the slag at $1300^\circ C$ cannot be greater than 0.05. Similarly FeO in the slag will be negligible. Thus oxidation of metal can be ruled out. As steel samples were obtained at the end of refining in the open hearth steel making, presence and oxidation of any silicon in the melt to give SiO_2 in the slag is also very unlikely. There can not be any chance of entrapped slag coming with the steel samples as they were first machined and remelted in the induction furnace to make the iron-carbon alloys.

Both manganese and sulphur are dissolved in the melt at higher temperature and as the temperature is lowered the equilibrium product of [Mn] [S] is lowered. Manganese and sulphur must react to form MnS which then floats to the surface. Nucleation of MnS inside the melt is essential for reaching equilibrium. Similarly iron and sulphur may react to form FeS, if the activity of FeS be lowered by its solution in MnS. Exact behavior of FeS – MnS system is not known, but if it is assumed to be ideal, a_{MnS} is likely to be close to unity. Formation of FeS can thus not explain the observed lowered values of sulphur in the melts compared to the theoritical values, especially in the melts having sulphur content less than 0.06 percent.

It can be concluded from the above that the consistent lower values of sulphur obtained at $1300^{\circ}C$ and $1400^{\circ}C$ compared with the theoretical values may be attributed to the higher activity coefficient of sulphur in the melt or to the higher equilibrium constant for the reaction (4.5), than the values reported in the literature. The equilibrium constant and the standard free energy of the reaction(4.5) are recalculated using the experimental data of the present investigation and the activity coefficient values of sulphur and manganese as calculated in Chapter 4. The calculated values of $\triangle G^{O}$ are compared with the reported values from equation (4.6) in Figure 7.3. The discrepancy is greater for samples taken at temperatures of $1300^{\circ}C$ and $1400^{\circ}C$ compared to these samples taken at $1200^{\circ}C$. At higher temperature, sulphur content is more which can lead to the formation of FeS in the slag. Probability of FeS and MnS to form solid or liquid solution is also more at higher temperatures. By taking a_{MnS} as mole fraction of MnS in the slag as explained in Chapter 4 the reported values of $\triangle G^{O}$ agree better with the recalculated values from the experimental data of the present study. In most of the cases at $1300^{\circ}C$ and $1400^{\circ}C$, discrepancy in the two values of $\triangle G^{O}$ is less than 1.8 kcal/mole which is within the accuracy of the reported data.
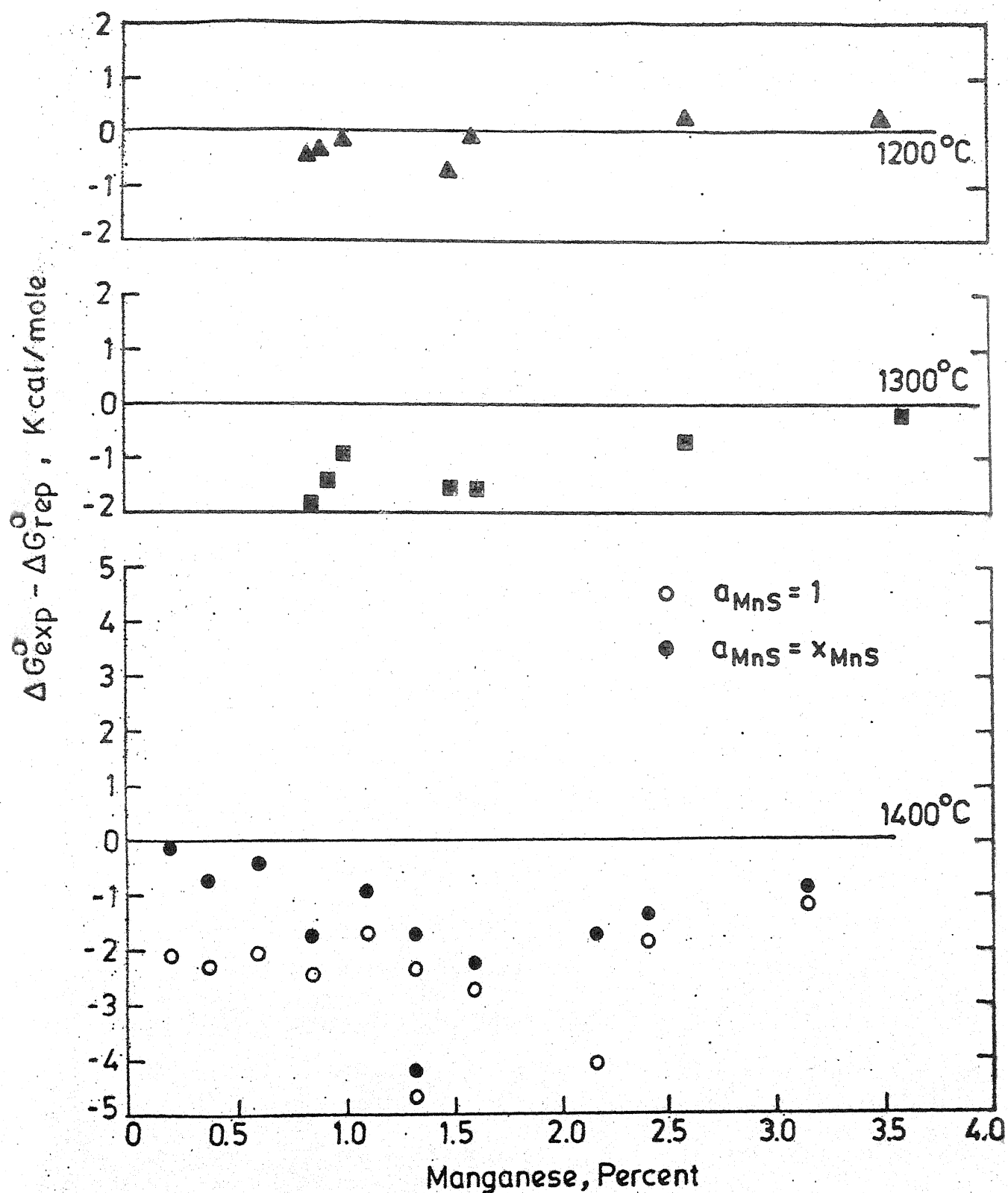
FIG. 7.3 PLOT SHOWING DISCREPANCIES IN THE EXPERIMENTALLY DETERMINED VALUES OF STANDARD FREE ENERGY OF FORMATION OF MnS FROM [Mn] AND [S] IN MELT.

7.1.2 Cooling and heating of the melt at the same manganese level

The sulphur analysis of the samples collected during cooling to $1200^{\circ}C$ and then heating back to $1300^{\circ}C$ revealed that there was some sulphur transfer from the slag to the metal during the reheating period. The sulphur level in such samples was always found to be lower than that of the samples taken during cooling of the melt. This discrepancy may be due to the fact that the sulphur transfer from the slag to the metal is sluggish as the quantity of MnS formed is very small and it may not be uniformly mixed with the melt during the mannual stirring by the graphite rod. The dissolution kinetics of MnS is not well understood but it may take more than one hour at $1300^{\circ}C$ to reach equilibrium with the melt. The fact that MnS in slag decomposes to approach equilibrium between the Mn and S levels in the melt

i.e. $MnS = \underline{Mn} + \underline{S}$
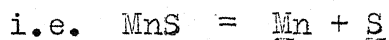
is confirmed by the results of the heat H_8, in Table 6.1.

Theoritically it is known that manganese and sulphur in the melt will react to form MnS in the slag as to reach equilibrium. However the quantity of slag formed was so small that it could not be collected and analysed easily. The quantity of slag formed in one case was deliberately increased by adding excessive amount of FeS and Mn to the charge materials in the crucible of heat H_9. In this case the slag could be collected after breaking the crucible at the end of the experiment. Comparison of X-ray diffraction

of this slag(Figure 6.4)with the X-ray diffraction file data
confirmed the presence of MnS. Presence of FeS or Fe phases
in slag was not noticed. Chemically it was analysed to
contain more than 35 pct. Mn and 20 pct S. The set up was
not geared to analyse such samples accurately so the results
can be subject to some errors. These findings however
confirmed the formation of MnS in the slag. This is also
confirmed from the results reported in Table 6.3 that sulphur
in melt decreases when manganese additions to melt at a
constant temperature. Attempts were also made to form MnS
in the laboratory by melting FeS and Mn materials in the
graphite crucibles. X-ray diffraction pattern of the product
Figure 6.2 marked the presence of MnS and some other phases.
X-ray diffraction patterns of locally procurred FeS and MnS
materials however did not give any clear picture regarding
the phases present in them. Exact chemical analysis of these
materials are also not known though they were analysed to
contain about 20 to 30 pct sulphur.

7.1.3 Approach to the equilibrium during furnace cooling of the melt

Attempts were made to simulate the plant conditions
where metal in the ladle cools without any external stirring.
When the melt was allowed to cool in the furnace under the
argon atmosphere by simply turning off the power of the
furnace, it took 10 minutes for the melt to reach $1300^{o}C$ and
another 5 minutes to reach around $1200^{o}C$. The sulphur
analysis of the samples collected from the cooling melt
is compared with the sulphur analysis of the samples from

the melt where equilibrium was allowed to reach by holding
the melt at that temperature for one hour or so, in
Figure 7.4. The temperature measurements of the cooling
melt may be slightly erroneous but the trend is towards
higher S values in the samples from the cooling melt. Still
a significant drop in the sulphur content during the cooling
of melt in 10-20 minutes of time is observed and it may be
quite significant from practical point of view. The sulphur
levels tend to reach the equilibrium values if the melt is
cooled slowly in the furnace by reducing the power to the
furnace such that it takes 40 and 80 minutes for the melt to
reach $1300^{o}C$ and $1200^{o}C$ respectively.

7.1.4 Model for calculating manganese and sulphur in the melt

A mathematical model based on manganese and sulphur
balances can be worked out to determine the manganese and
sulphur contents of the melt under certain equilibrium
conditions. Let the quantities of FeS, MnS and Mn, in gms
added to 100 gms of Fe-C alloy be expressed as X_1, Y_1 and Z_1
respectively. If X_2 gm of FeS and Y_2 gm of MnS decompose to
give Fe, Mn and S to the melt, the final quantity of the
molten alloy will be $(100 + X_2 + Y_2 + Z_1)$. Similarly slag
quantity will be $(X_1 + Y_1 - X_2 - Y_2)$ gms and percentage of
manganese and sulphur in the molten alloy can be written
as follows;

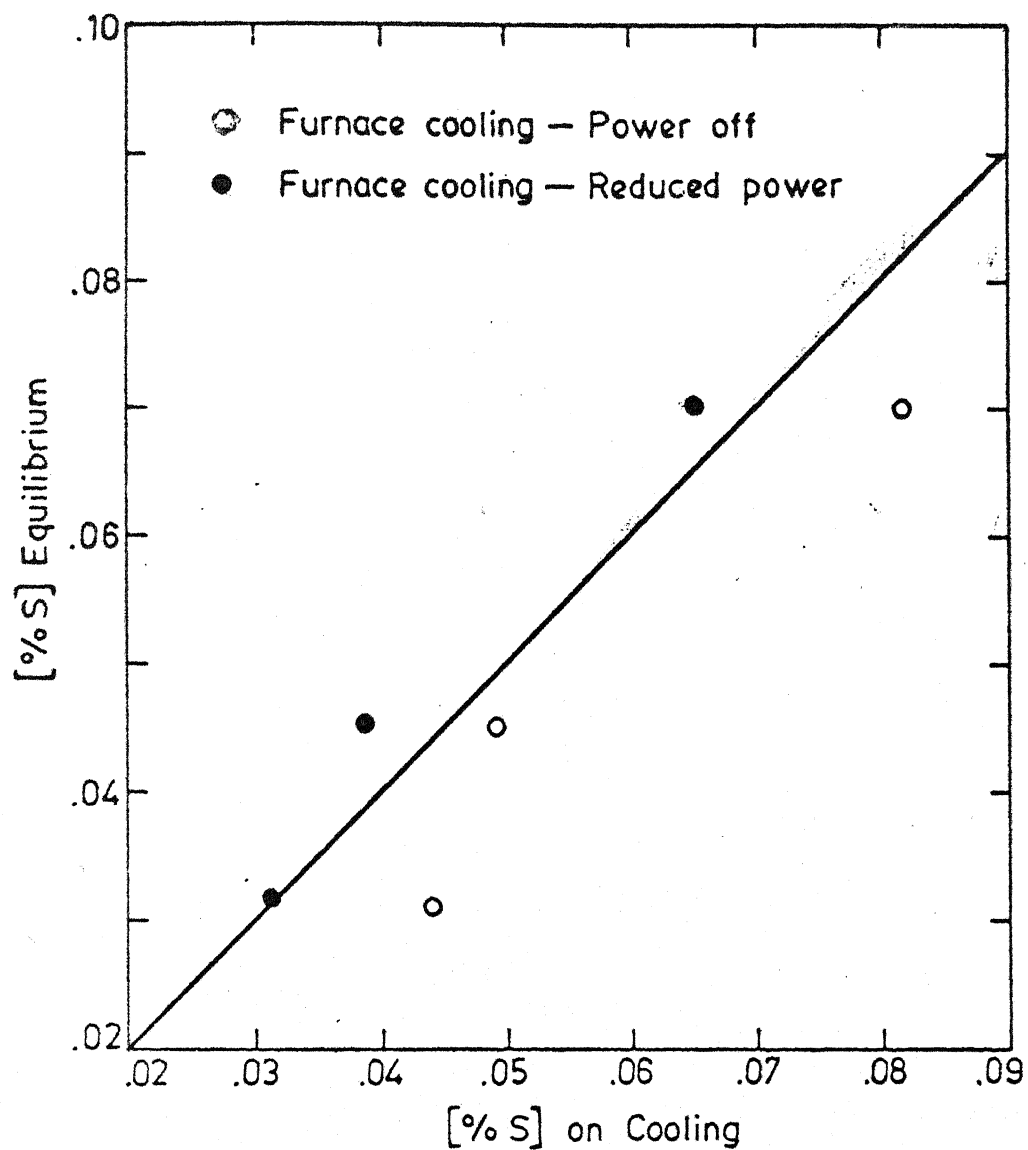$$[Mn] = \frac{\frac{55}{87} Y_2 + Z_1}{100 + X_2 + Y_2 + Z_1} \times 100 \qquad (7.4)$$

FIG. 7.4 PLOT SHOWING APPROACH OF EQUILIBRIUM DURING COOLING FROM 1400°C.

$$[S] = \frac{32 \frac{X_2}{88} + \frac{Y_2}{87}}{100 + X_2 + Y_2 + Z_1} \times 100 \qquad (7.5)$$

Assuming ideal behavior of FeS and MnS in the slag, the equilibrium constants for reactions (4.5) and (4.15) can be written as follows;

$$K_{4.5} = \frac{X_{MnS}}{f_{Mn} \, f_S [Mn] \, [S]} \qquad (7.6)$$

$$K_{4.15} = \frac{X_{FeS}}{f_S [S]} \qquad (7.7)$$

The mole fraction of MnS and FeS can be assumed to be same as their weight fraction and can be written as follows;

$$X_{MnS} = \frac{Y_1 - Y_2}{X_1 + Y_1 - X_2 - Y_2} \qquad (7.8)$$

$$X_{FeS} = \frac{X_1 - X_2}{X_1 + Y_1 - X_2 - Y_2} \qquad (7.9)$$

Values of $K_{4.5}$ and $K_{4.15}$ at any temperature can be known from the data given in Chapter 2 or 4. To compute the values of X_2 and Y_2 equations (7.6) to (7.9) can be solved. Then the percentage of mangane and sulphur in the melt can easily be computed by using equations (7.4) and (7.5).

For example using experimental data of heat H_9 manganese level in melt was calculated to be around 0.1 pct and the sulphur level as 1.17 pct from the above model. The calculated value agreed with the experimentally determined . sulphur content of 1.07 pct. Similarly for heats H_1 to H_7

calculations showed that manganese should react with added
FeS to form MnS and the final Mn in the alloy would be
0.2 to 0.6 pct less than the value calculated from the
manganese additions to the charge. In case of heats H_{13} and
H_{14} local grade of MnS and FeS were used, the [Mn] and [S]
levels calculated from the above model did not match well
with the experimental values as shown in Table 7.1. The
only source of manganese and sulphur in the alloy melt was
MnS in heat H_{13} as no manganese or FeS was added in the
charge mix of the crucible. Some MnS might decompose to
give manganese and sulphur in the alloy melt and some MnS might
react with Fe to form FeS and manganese. Thus the ratio
of manganese and sulphur in the alloy melt should be greater
than the stoichiometric ratio of 55:32 where as actual Mn:S
ratio of 1.06 was obtained. This was possible if some sulphur
was present in some other form e.g. MnS_2, FeS, free sulphur etc.
in the charge material.

7.2 Slag-Metal Equilibrium

7.2.1 Effect of slag basicity on sulphur levels of the melt

The effect of slag basicity for manganese free metal
on its sulphur level is plotted in Figure 7.5 based on the
experimental data of Chapter 6. As the basicity of the slag
i.e. (CaO/SiO_2 ratio) increases, the desulphurisation of the
metal increases. This agrees with the findings of many other
investigators.[15] Increasing the slag quantity has also helped
in decreasing the sulphur level of the melt. Corresponding
calculations for the sulphur partition ratio and comparison

Table 7.1

Comparison of Theoritical and Experimental [Mn] and [S] Levels at $1400^{\circ}C$

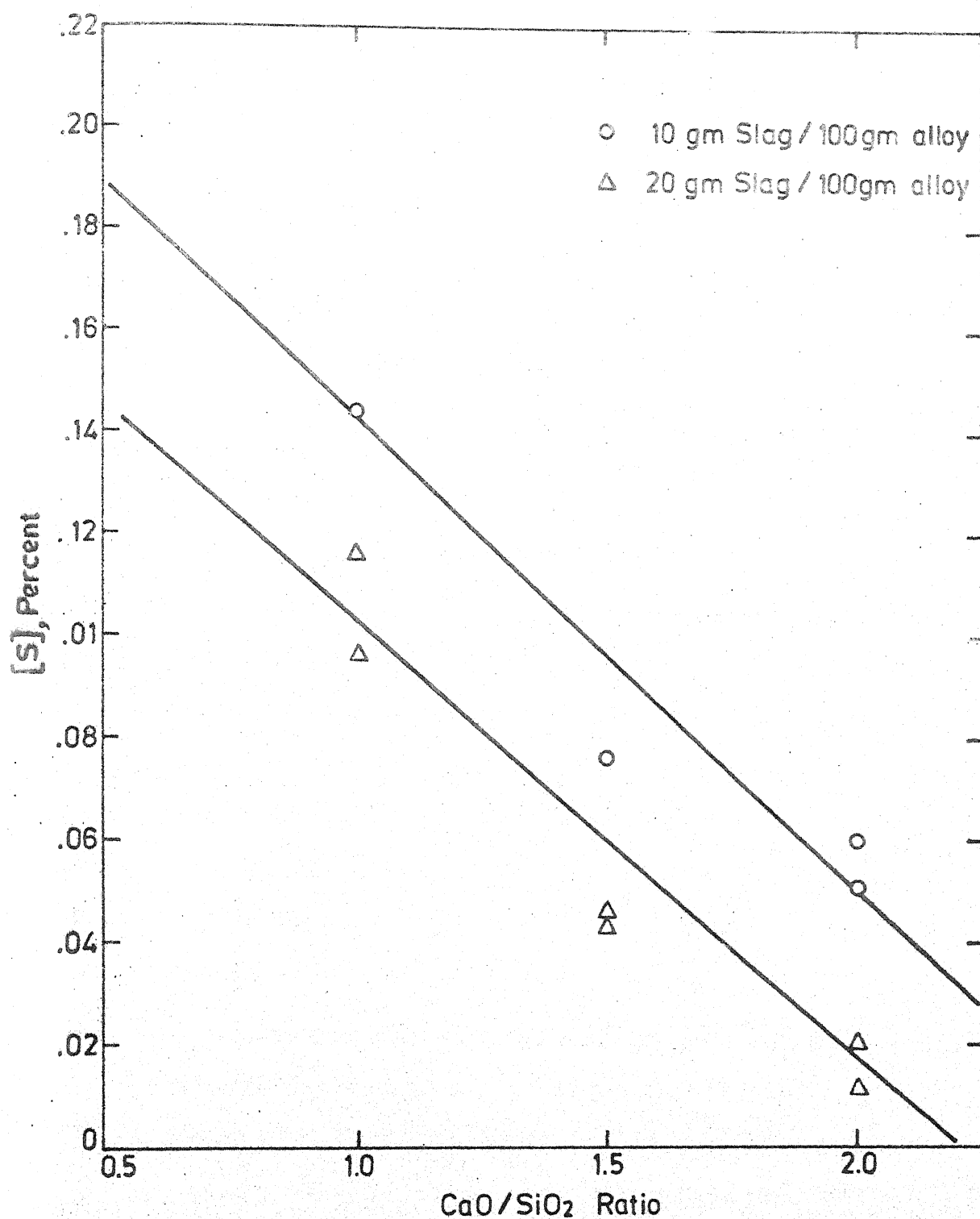| Heat No.	Sample No.	pct. Mn		pct. S	
		Theoritical	Expt.	Theoritical model $a_{Mns} = X_{MnS}$	Expt.
	$H_{13}-S_1$	0.955	0.371	0.188	0.347
	$H_{13}-S_2$	1.910	1.320	0.099	0.110
H_{13}	$H_{13}-S_3$	2.840	2.160	0.065	0.069
	$H_{13}-S_4$	2.760	3.140	0.051	0.057
	$H_{14}-S_1$	0.162	0.200	0.734	0.680
	$H_{14}-S_2$	0.350	0.600	0.450	0.230
H_{14}	$H_{14}-S_3$	0.660	1.320	0.276	0.095
	$H_{14}-S_4$	1.150	2.160	0.160	0.064

FIG. 7.5 EFFECT OF SLAG BASICITY (CaO/SiO₂ ratio) ON THE DESUL-
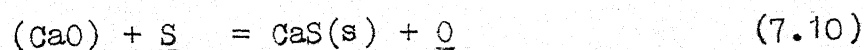FURISATION OF CARBON SATURATED IRON AT 1400°C.

with the theoritical value are described later.

7.2.2 Effect of manganese on sulphur levels of the melt

At 1400°C as the manganese level in the metal increases, the sulphur level decreases in almost all cases as shown in Figures 7.6 to 7.9 for different compositions and volumes of the slag.

It has been discussed in Chapter 4 that the sulphur level of metal should decrease with decreasing a_{MnS}. MnS formed in presence of Mn in the melt will lower its activity by becoming a part of the slag. Transfer of manganese from metal to slag phase was confirmed by the chemical analysis of the slag in a few cases. Actual transfer of manganese from metal to slag can result due to the formation of MnS or MnO as per equations (4.5) and (2.34). X-ray diffraction of the slag (Figure 6.4) did not confirm the presence of MnS or MnO phases probably due to small quantity of MnS or MnO in the slag or because they may be present in some other form. The role of manganese in lowering the sulphur level can be attributed to any of the following;

(1)   Manganese reacts with sulphur to form MnS and activity of MnS is lowered by its solution with the oxide slag.

(2)   Manganese enhances the rate of sulphur removal by CaO in the slag as per the following reactions;

$$(CaO) + \underline{S} = CaS(s) + \underline{O} \qquad (7.10)$$

$$\underline{O} + \underline{Mn} = (MnO) \qquad (7.11)$$

FIG. 7.6 EFFECT OF MANGANESE IN CARBON SATURATED IRON
ON THE DESULPHURISATION OF THE MELT AT 1400°C
AND SLAG BASICITY (CaO/SiO₂ Ratio) OF ONE.

FIG. 7.7 EFFECT OF MANGANESE IN CARBON SATURATED IRON ON THE DESULPHURISATION OF THE MELT AT 1400°C AND SLAG BASICITY (CaO/SiO₂ Ratio) OF 1.5.
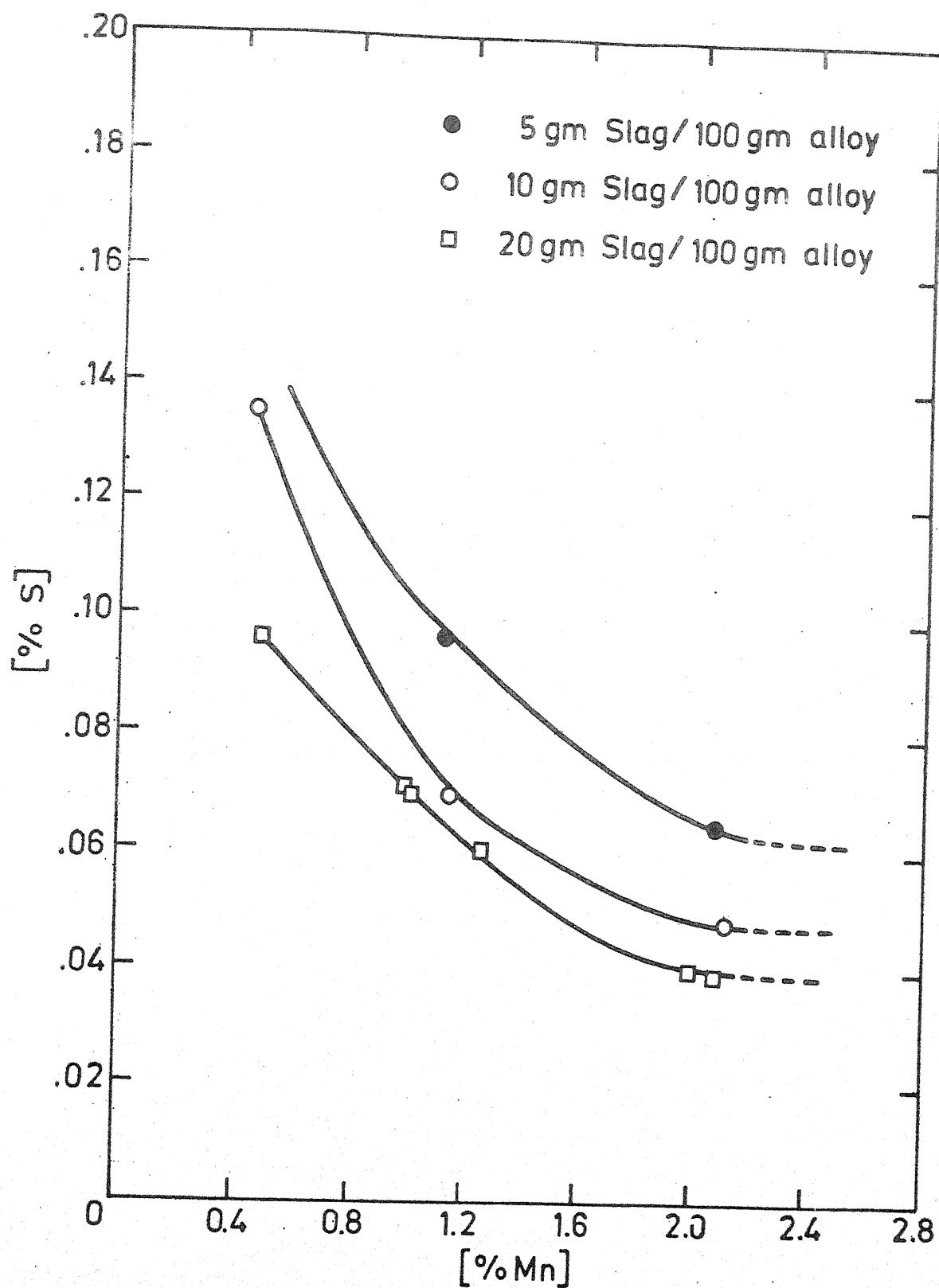
FIG. 7.8 EFFECT OF MANGANESE IN CARBON SATURATED IRON ON THE DESULPHURISATION OF THE MELT AT 1400°C AND SLAG BASICITY (CaO/SiO$_2$ Ratio) OF 2.0 .
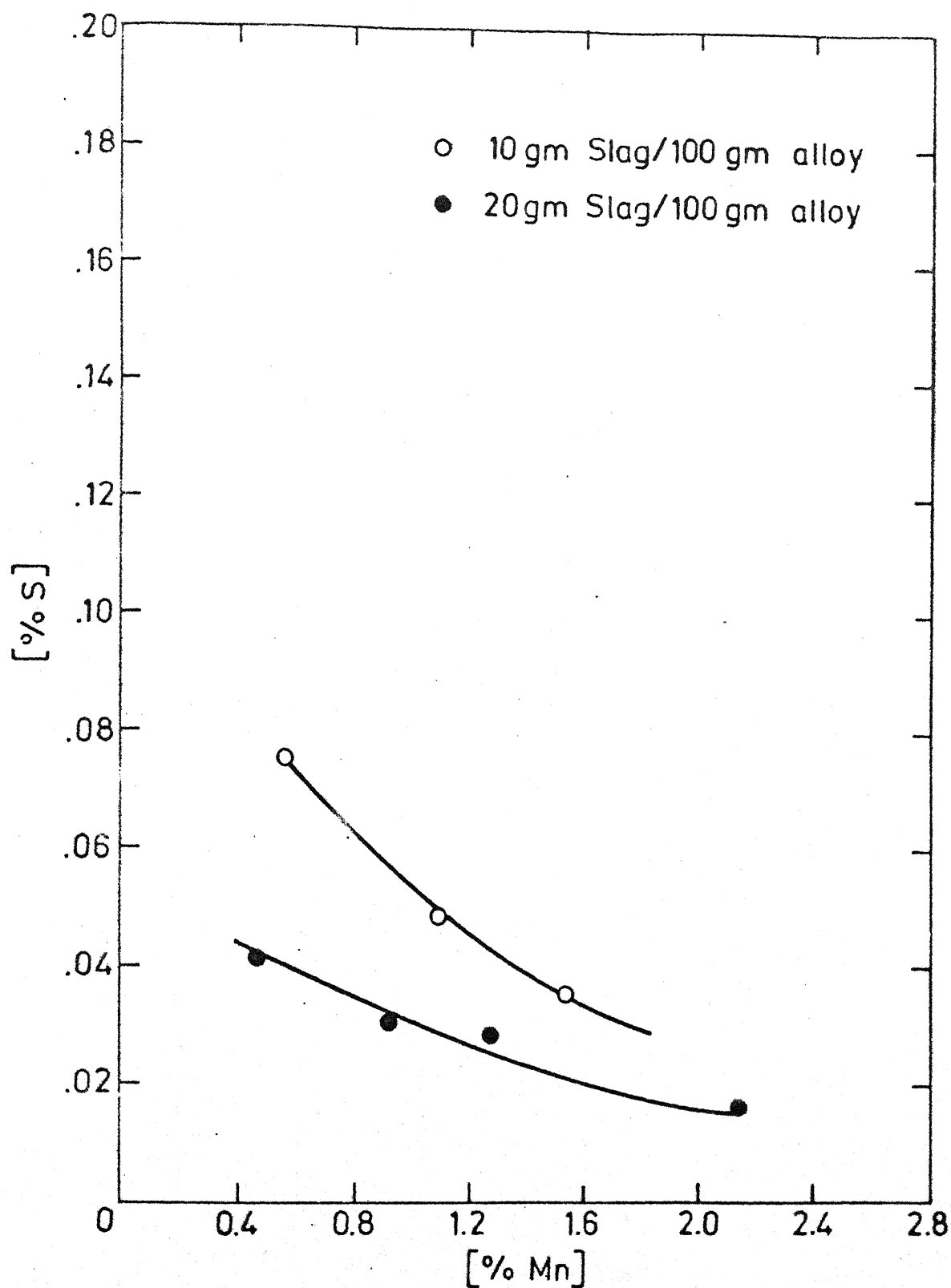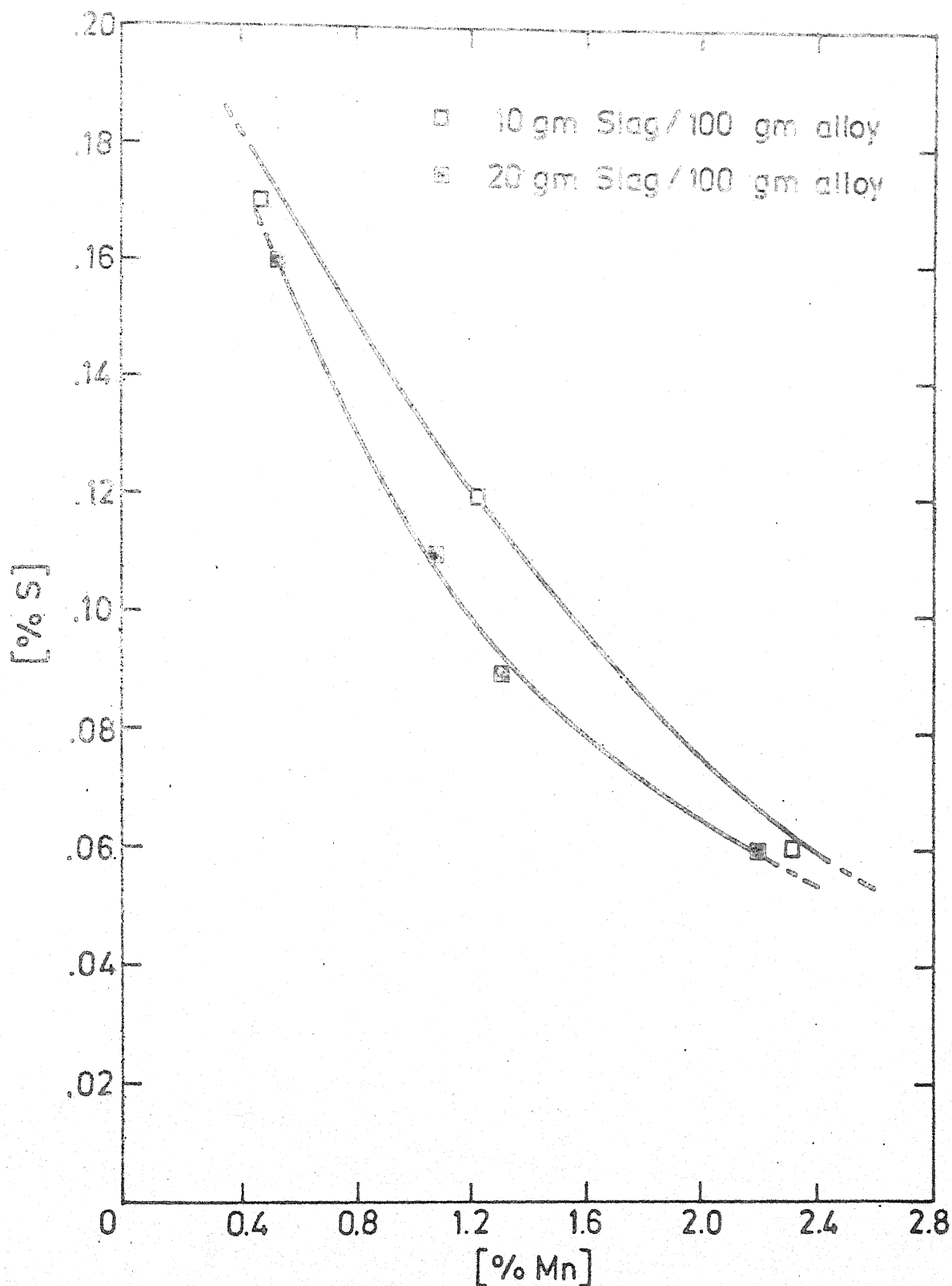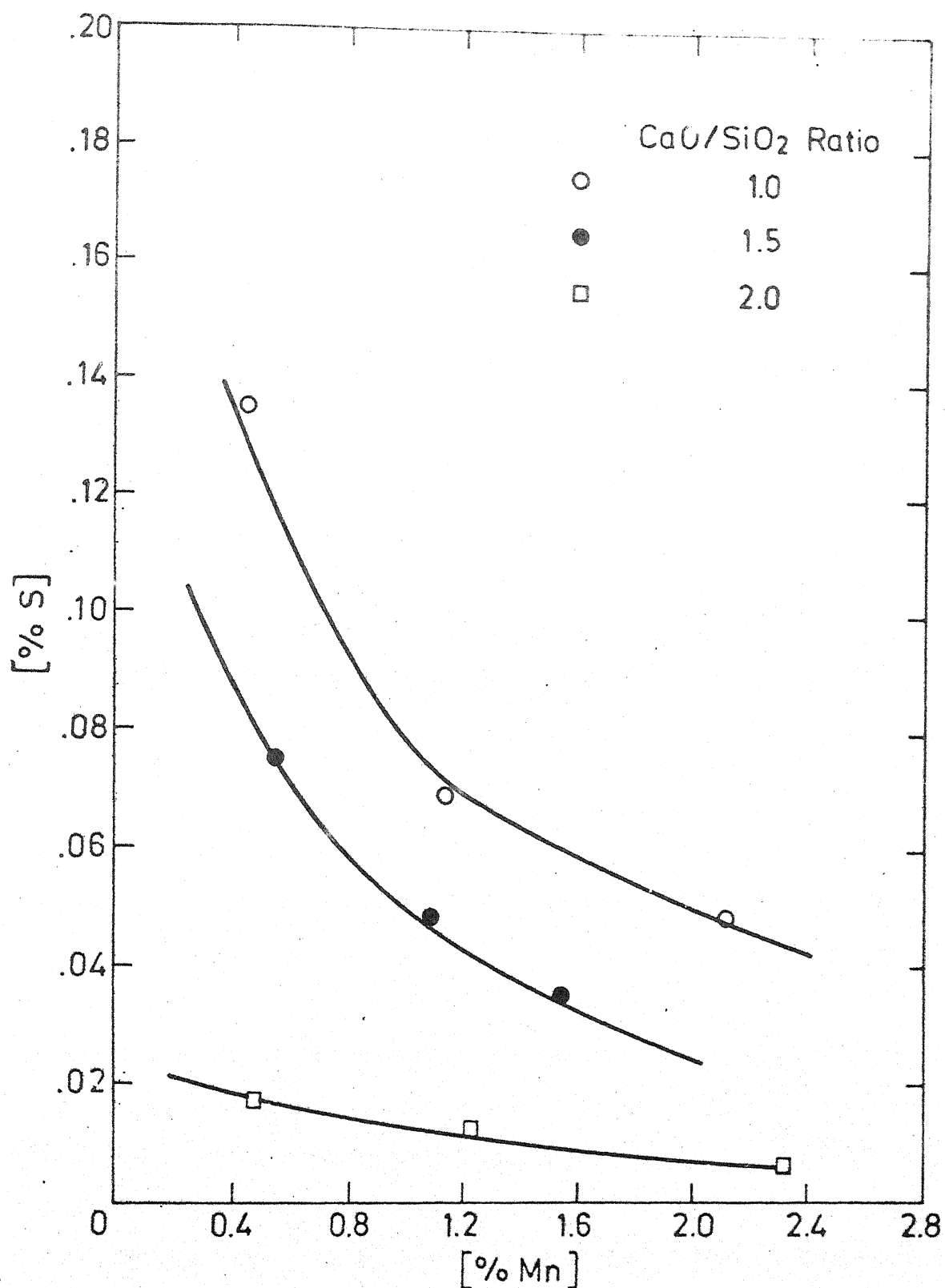
FIG. 7.9 EFFECT OF MANGANESE IN CARBON SATURATED IRON
ON DESULPHURISATION OF THE MELT, CONTAINING
10 gm SLAG/100 gm OF ALLOY, AT 1400°C.

(3)   Manganese in melt reacts with SiO_2 in slag to form silicon in the melt and MnO in slag as per reaction (2.34). This would increase slag basicity and hence favor sulphur removal.

It is possible all the three factors may be responsible for the lowering of sulphur level in presence of manganese in the melt. The probable reactions occuring in the system are further discussed in the following section.

7.2.3 Multi component-multiphase model

The probable reactions in the multi component system can be described by reactions (7.12) to (7.17) which are rewritten in Table 7.2. The standard free energies and equilibrium constants of these reaction can be determined from the thermodynamic data given in Chapter 2 and are included in Table 7.2.

At slag metal interface p_{CO} can be assumed to be one atm. If silicon and manganese levels are at equilibrium with respect to MnO and SiO_2 in the slag by reactions (7.12) and (7.13) respectively then reaction (7.15) can describe the over all sulphur transfer from metal to slag. If reduction of oxides by carbon are ignored, silicon content in the metal will be given by reaction (7.14) and sulphur transfer can be described by reactions (7.16) or (7.17). If the reduction of SiO_2 by manganese is sluggish the sulphur transfer can be described by reaction (7.12) only. If SiO_2 in slag is reduced by carbon to give silicon in metal then

Table 7.2

Summary of the Reactions for Multicomponent Multiphase Model

Sl. No.	Reaction	Equation No.	ΔG^o Cal.
1	$(SiO_2)+2C(gr)=[Si]_{Wt\%}+2\ CO(g)$	(7.12)	$145100\ -95.55\,T$
2	$(MnO)+C(gr)=[Mn]_{Wt\%}+CO(g)$	(7.13)	$68962.8-49.80\,T$
3	$(SiO_2)+2[Mn]_{Wt\%}=[Si]_{Wt\%}+2(MnO)$	(7.14)	$7175\ +4.06\,T$
4	$(CaO)+[S]_{Wt\%}+C(gr)=CaS(s)+CO(g)$	(7.15)	$27465.7-27.12\,T$
5	$(CaO)+[S]_{Wt\%}+[Mn]_{Wt\%}=(CaS)+(MnO)$	(7.16)	$-41495.6+22.62\,T$
6	$(CaO)+[S]_{Wt\%}+\frac{1}{2}[Si]_{Wt\%}=(CaS)+\frac{1}{2}(SiO_2)$	(7.17)	$-45083\ +20.65\,T$

$$K_{7.12} = \frac{f_{Si}\ [Si]\ p_{CO}}{\gamma_{SiO_2}\ X_{SiO_2}\ a_C} \qquad (7.18)$$

Taking $f_{Si} = 15$ and $p_{CO} = a_C = 1$, and replacing the mole fraction of SiO_2 by its weight fraction, then equation (7.18) will be simplified to the following form;

$$K_{7.12} = \frac{1500\ [Si]}{\gamma_{SiO_2}(Wt\ \%\ SiO_2)} \qquad (7.19)$$

The equilibrium sulphur level in this case will be governed by the following equation;

$$\frac{(S)}{[S]} = 4\ \left(\frac{\gamma_{CaO}}{\gamma_{CaS}}\right)\ (Wt\%\ CaO)\ K_s \qquad (7.20)$$

γ_{SiO_2} and $\frac{\gamma_{CaO}}{\gamma_{CaS}}$ are known to vary with slag basicities as mentioned in Chapter 2. As reduction of SiO_2 of carbon proceeds, slag basicity will increase which will lower γ_{SiO_2} and increase $\frac{\gamma_{CaO}}{\gamma_{CaS}}$ ratio. Equilibrium between slag and metal will be reached at a particular basicity greater than the initial basicity of the slag. If 'f' is weight fraction of slag added to the melt having basicity of B_1 with 20 pct. Al_2O_3 and x gms of SiO_2 react with carbon to form Si in 100 gms of melt, then;

$$Si = \frac{28}{60}\ x\ ,\ gm \qquad (7.21)$$

$$SiO_2\ left\ in\ the\ slag = \frac{80\ f}{1 + B_1} - x\ ,\ gm \qquad (7.22)$$

$$CaO\ in\ slag = 80\ f\ \frac{B_1}{1 + B_1}\ ,\ gm \qquad (7.23)$$

Total slag after SiO_2 reduction

$$= 100 \; f - x \qquad\qquad (7.24)$$

The CaO/SiO_2 ratio can now be written as follows;

$$\frac{CaO}{SiO_2} = \frac{80 \; f\dfrac{B_1}{1+B_1}}{\dfrac{80 \; f \; B_1}{1 + B_1} - x} \qquad\qquad (7.25)$$

Equation (7.25) can be simplified to :

$$\frac{CaO}{SiO_2} = \frac{1}{1 - \dfrac{(1+B_1)x}{80 \; f \; B_1}} \qquad\qquad (7.26)$$

Knowing γ_{SiO_2} as function of $\dfrac{CaO}{SiO_2}$, value of x can be

determined for equation (7.18). Calculations show that

slag volume of 20 pct and basicity of 1.0, 1.21 gms of

SiO_2 will be reduced to give 0.56 pct. Silicon in metal

and final CaO/SiO_2 ratio 1.2 in the slag. At slag basicity

of 1.2, $\dfrac{(S)}{[S]}$ ratio is calculated to be around 80 at $1400^{o}C$

from equation (7.20) which is plotted in Figure 2.6. Corres-

ponding sulphur level in melt should be 0.025 for slag volume

of 20 pct as calculated from equation (1.2). The experimental

values of sulphur level in metal obtained for this combination

of slag volume and composition were much greater than the

equilibrium value of 0.025 pct. The equilibrium sulphur

is not influenced by the addition of manganese to the melt.

The equilibrium constant of SiO_2 reduction by manganese in

the melt (reaction 7.14) is given as follows;

$$K_{7.14} = \frac{\gamma_{MnO} \left(\dfrac{Wt\% \, MnO}{110}\right) 15 \, [Si]}{0.8 \, [Mn]^2 \, \gamma_{SiO_2} (Wt\% \, SiO_2)} \times 100 \qquad (7.27)$$

$[Mn] / (MnO)$ ratio is calculated to be around 1.0 at slag basicity 1.2 and $1400^\circ C$. For 1.2 pct manganese in metal MnO in slag will be around 1 to 2 pct and it can not thus influence the reactions (7.12) and (7.16) much due to corresponding changes in values of γ_{SiO_2}, $(\% \, SiO_2)$, $\gamma_{CaO}/\gamma_{CaS}$ or $(\% \, CaS)$ in the slag. Manganese may thus be helping to enhance the rate of either silica reduction by carbon or the sulphur transfer from the metal to slag towards the equilibrium value. This aspect has not been fully studied in the present work but it is in agreement with the findings of Turkdogan and other investigators. At higher slag basicity of 1.5 and 2.0 and with pure lime as desulphuriser the equilibrium sulphur levels will be also much lower than the values obtained experimentally. There also manganese may be helping in only increasing the rate of sulphur transfer from metal to the slag. The formation of MnS by the reaction between manganese and sulphur is also unlikely because the experimental data correspond to $a_{MnS} = 0.30$ at slag basicity 1.0 and slag volume of 20 pct. Total MnS formed by the addition of manganese to the melt can not be greater than 1.0 pct.of the slag. More over a_{MnS} values calculated from the data of manganese and sulphur in the melt does not increase with increase in manganese content of metal which can be expected if MnS is formed to lower sulphur in metal. Activities of MnS in slag are

calculated to be 0.15 and 0.05 at slag basicities of 1.5 and 2.0. For manganese and sulphur reaction to occur, MnS must lower its activity by its immediate solution with slag. This will require much greater stirring than obtained in the present study.

It may also be possible that experimental results are subject to error due to improper sampling in presence of large quantity of slag. To check this samples were collected at the end of experiment from the solidified mass in the crucible. The experimental results in Table 6.6 confirm that equilibrium conditions are not reached in such experiments also. Hence manganese may be helping just to increase the rate of sulphur transfer from metal to slag phase. This aspect however is not confirmed by the results of heats H_{28} and H_{29} in Table 6.5. Therefore the role of Mn on the desulphurisation of the iron – carbon melt by the oxide slags of $CaO-SiO_2-MnO$ is not well understood yet and further work is needed in this area.

7.3 Industrial Applications

Equilibrium sulphur level of metal in presence of manganese decreases rapidly with increase in manganese content of metal or decrease in temperature. At $1300^{o}C$ and 2 pct. manganese, equilibrium sulphur value is around 0.058 pct. In the laboratory near equilibrium value i.e. 0.048 is reached in 10 minutes of cooling from $1400^{o}C$ without stirring the bath. Cooling to $1200^{o}C$ in 5 minutes decreases sulphur content to 0.044 pct. Thus reaction between manganese

and sulphur to form MnS product is quite fast and one can expect significant drop in sulphur content of metal of the ladle in cooling slowly during the transit from blast furnace to mixer. Data from Rourkela Steel Plant clearly shows this trend of lowering of sulphur content of metal (Figure 2.11). Presence of blast furnace carry over slag with the metal can not be ruled out and it may favor sulphur removal by manganese to form MnS as activity of MnS may be lowered. The kinetics of sulphur transfer to the oxide slag in presence of manganese without stirring the melt has not been yet studied but the equilibrium value of sulphur is much lower than found experimentally in the laboratory condition or found in the plant data.

Iyengar et al[40] reported that Rourkela Steel Plant developed a norm of hot metal manganese of 1.8 pct. for obtaining bath (steel) sulphur of around 0.030 pct. Sulphur in mixer metal would be around 0.035 pct. Equilibrium data shows that temperatures for this combination of manganese and sulphur in the hot metal is around $1220^{o}C$ which may be very close to the actual temperature of mixer metal though no measurements have been reported. The metal depth in the ladle or in the mixer may be 2-3 m. and in absence of stirring pure MnS must be formed by the reaction between manganese and sulphur inside the melt. Only at the slag metal interface MnS can lower its activity by its solution in slag. Diffusion of manganese and sulphur to the slag metal interface will be very slow to account for any significant drop in sulphur. Further drop may be possible only with good stirring of the melt.

CHAPTER VIII

SUMMARY AND CONCLUSIONS

Studies on sulphur control in iron making and steel making processes or by means of external treatment of metal in recent years have gained importance to meet challanges for production of low sulphur steel at lower cost for newer and newer applications in space, ocean, defence etc. Thermodynamics of sulphur reactions and desulphurising powers of various blast furnace and steel making slags have been investigated by many workers by equilibrating the melt with known H_2/H_2S ratio or with a known quantity and composition of slag at a fixed temperature. In the present work attempts have been made to investigate the effect of manganese on the desulphurisation of iron-carbon melts due to formation of MnS with and without addition of some oxide slags.

Theoretical models have been proposed to calculate the sulphur content of metal as function of temperature and manganese content of metal from the reported thermodynamic data on standard free energies of formation and heats of solution. Values of activity coefficients of sulphur in iron-carbon alloys in temperature range of 1200° to $1400^o C$ have been calculated, using a regular solution model, from the reported data at $1600^o C$. The experimental results of many investigation such as Oelsen, Sherman and Chipman, Morris etc. agreed with results of theoretical calculations. For sulphur

levels greater than 0.10 pct, both FeS and MnS may be formed
in the slag whereas at lower values of sulphur, MnS is the
predominant phase of the slag. In the present work FeS and
MnS are assumed to behave ideally.

The experiments were conducted in a silicon carbide
furnace under the neutral atmosphere of argon. The charge
materials were put in a graphite crucible for melting in the
furnace.

The calibrated thermocouples were used to measure the
temperature of the crucible just above the melt accurately.
Drawing alloy samples by quartz tube did not pose any problem.
In a few cases samples were taken from the solidified alloy
mass at the end of the experiment.

The set up for sulphur analysis of the alloy was
calibrated with standard steel samples obtained from BCS
and hence the results of analysis are considered to be quite
accurate. The purity of the charge materials was checked by
the X-ray diffraction and chemical analysis. All materials
except locally procured FeS and MnS were found to be free
of impurities.

Equilibrium in the Fe-C-Mn-S system was checked by
drawing samples at about 1300°C both during cooling and
heating cycles. The equilibrium was more or less reached
in one hour duration at constant temperature.

Additional experiments were carried out to study the
approach to the equilibrium during cooling of the melt without
any stirring as to simulate the conditions in the ladle during

transit from the blast furnace section to the steel making section. Near equilibrium values of manganese and sulphur levels in melt were obtained in such experiments. To check whether MnS is formed in the experiments, one slag sample was chemically analysed to contain high manganese and sulphur. This was further confirmed by the presence of MnS phase in the X-ray diffraction pattern.

In some experiments manganese was added to the melt in steps at a fixed temperature. The lower content of the manganese in the melt than that of the charge suggested that maganese had reacted with sulphur in the melt to form MnS. However the formation of FeS in the slag at higher temperatures could not be ruled out.

Comparison of theoritical values of sulphur contents in carbon saturated metal at different temperature and manganese content of metal with the experimental results of present work shows that good agreement is reached in most of the cases if the activities of MnS and FeS in slag are taken same as their weight fractions and a discrepancy of $- 1.0$ to -1.8 KCal/mole in the reported standard free energy of formation of MnS is allowed. These limits are within the accuracy of the reported data.

From slag metal equilibrium studies for 4-6 hours at $1400^{\circ}C$, it is found that manganese up to 2 pct. decreases the sulphur content of metal at all combinations of slag volume (10 to 20 pct.) and slag basicity (Cao/SiO_2 ratios, 1 to 2).

A multicomponent multiphase model is proposed to study the approach of the system towards equilibrium. Reduction of SiO_2 in the slag by carbon or manganese in the melt occurs, increasing there by the basicity of slag. For a melt having slag volume of 20 pct. and basicity of 1.0, 1.21 gms of SiO_2 is reduced to give 0.56 pct. of Si in metal and $\frac{CaO}{SiO_2}$ ratio of 1.2 in the slag. For this slag basicity, the sulphur equilibrium partition ratio is around 80 and equilibrium sulphur content is 0.025 pct. The actual values are higher than this but they tend to reach equilibrium value with increasing manganese content of metal. Equilibrium and actual sulphur content of metal decreases with increase in slag volume or increase in slag basicity. The exact role of manganese in lowering of sulphur level in the melt in presence of oxide slag however could not be properly understood from the findings and experimental results of this work. More experiments and complete analysis of metal and slag samples are needed and recommended to gain further understanding of Mn-S interactions in the Fe-C alloys.

CHAPTER IX

SUGGESTIONS FOR FURTHER WORK

Difficulties were faced for procurement of pure
manganese sulphide material . The manganese sulphide
procured locally contained lot of unidentified impurities.
Hence it is suggested that attempts should be made for
preparation of manganese sulphide and iron sulphide in the
laboratory by some suitable methods such as synthesising
pure manganese and pure sulphur under vacuum around $250^{\circ}C$.

Basic studies by addition of MnS to iron-carbon melt
may be necessary to understand its decomposition behavior in
the melt and give an independent confirmation of manganese
sulphur equilibrium in the Fe-C-Mn-S melt.

In order to explain the effect of manganese
on desulphurisation in presence of oxide slags, synthetic
slags such as $MnS-CaO-SiO_2-Al_2O_3$ and $FeS-CaO-SiO_2-Al_2O_3$
should be prepared in the laboratory for studying slag-
metal equilibrium.

Further experiments may be planned for equilib-rating
the Fe-C-Mn melts with known H_2/H_2S ratio at fixed temperatures.
H_2/H_2S ratio of H_2 and H_2S gas mixture will correspond to a
particular sulphur concentration in the melt at equilibrium
and this in turn will correspond to a particular manganese
content of metal. The final manganese content of the alloy
melt can thus be compared with the theoretical value of

manganese-sulphur equilibrium calculations. The starting
manganese in the melt must be kept greater than the
equilibrium value for such experiments.

It is desirable to have access to complete and
accurate analysis of slag and metal for better correlations
of the thermodynamic data and comparison with predicted
values.

Experimental data is also needed for melts containing
carbon other than saturation values. This may be possible
in the pure Al_2O_3 crucibles.

There is also need to get more scientific and reliable
data from the industry.

Temperature of blast furnace metal and slag, accurate
analysis of blast furnace metal and slag, ladle metal
temperature and analysis, mixer metal and mixer slag analysis,
mixer temperature are needed to correlate the industrial
data with laboratory study. Industrial data of desulphurisation
of iron with additions of pure lime, slags and carbides in
presence of manganese in the metal will also be helpful in
analysis of data.

REFERENCES

1. Biswas, A.K., Principles of Blast Furnace Iron Making, (1981), Cootha Publishing House, Brisbane, Australia, p. 350.

2. Flint, R.V.; B.F. - S.P. 50 No.1, (Jan. 1962), p. 47-58, p. 74-76.

3. Wentrup, H.; Iron and Steel Inst. Carnegie Scholarship Memoirs (1935), 24, p. 103.

4. Holbrook, W.F. and Joseph, T.L.; Trans. AIME (1936), 120, p. 99.

5. Holbrook, W.F.; Trans. AIME (1938), 131, p. 127.

6. Oelsen, W.; Stahl und Eisen, (1948), 68, p. 175-186.

7. Sherman, C.W. and Chipman, J.; Trans. AIME, (June 1952), Jn. of Metals, p. 597.

8. Sherman, C.W., Elvander, H.I. and Chimpan, J.; Trans. AIME (1950), 188, p. 334.

9. Morris, J.P. and Williams, A.J.; Trans. ASM, (1949), 41, p. 1425.

10. Morris, J.P. and Buehl, R.C.; Trans. AIME (1950), 188, p. 317.

11. Basic Open Hearth Steel Making; AIME, New York, (1944).

12. Ban-Ya, S. and Chipman, J.; Trans. AIME, 242 (May 1960), p. 940.

13. Kitchener, J.A.; Bockris, J., and Liberman, A.; Discussions of the Faraday Society, No. 4 (1948).

14. Morris, J.P.; Jn. of Metals (September 1952), p. 939-940.

15. Hatch, G.G. and Chipman, J.; Trans., AIME (1949), 185, p. 274.

16. Derge, G., Philbrook, W.O. and Goldman, Kenneth. M.; Trans. Met. Soc. AIME, (1950), 180, p. 1111.

17. Ramachandran, S., King, T.B. and Grant, N.J.; Op. Cit.; (1956), 206, p. 1549.

18. Chang, L.C. and Goldman, K.M., Op. Cit.; (1948), 176 , p. 309.

19. Ward, R.G. and Salmon, K.A.; J. Iron Steel Inst., (1980), 196 , p. 393-403.

20. Saito, T. and Kawai, Y.; J. Jap. Inst. Met., (1955), 19 , p. 170.

21. Hatano, M.; Tetsu-to-Hagane, (1969), 55 , p. S704.

22. Yoshi, G.; Ibid., p. S701.

23. Tokuda, M. and Ohtani, M.; Ibid, p. S708.

24. Frohberg, M.G., Papamantellos, D. und Hanert, D.; Arch Eisenhuttenw; (1969), 40; p. 15.

25. Neuhaus, H., Langhammer, H.J., Geck, H.G. und Shenk, H.; Stahl u. Eisen, (1965), 85, p. 1578.

26. Turkdogan, E.T., Met. Trans.; (1978), 9B , p. 163-178.

27. Sharma, R.A. and Richardson, F.E.; JISI (1962), 200 , p. 373.

28. King, T.B. and Ramachandran, S.; Physical Chemistry of Steel Making; Ed. J.F. Elliot, John Wiely, New York (1958).

29. Electric Furnace Steel Making, Ed., SIMS, C.E.; AIMMPE, (1967).

30. Sigworth, G.K. and Elliot, J.F.; Met. Sci. (1974), 8 , p. 298.

31. Elliot, J.F., Gleiser, M. and Ramakrishna, V.; Thermochemistry of Steel Making, (1963), Vol.2, p. 525, Reading Mass. Addison-Wesley.

32. Kawai, Y. and Mori, K.; Trans Iron Steel Inst., Japan, (1973), 13 , p. 303.

33. Young, D.J. and Cripps Clark, C.J.; IMSM, (1980), 5 , p. 209.

34. Ohtani, M.; Sci Rep. Res. Inst.; Tohuku Univ., Ser.A.; (1957), 9 , p. 426-433.

35. Shenk, H. and Neumann, F.; Archiv Eisenhuttenw, (1958), 29 , p. 263-267.

36. Batra, N.K.; Proceedings of All India Seminar on Extraction of Iron, Bhilai Steel Plant, India, (1984), p. III-21.

37. Shibata, Z.; Tech. Report. Tohoku Imp. Univ. Tokio, (1928), 7 , p. 279/89.

38. Jensen, E.; J. Amer, Sci., (1942), 240, p. 695/709.

39. Meyer, D. and Shulte, F., Archiv fur das Eisen huttenwesen, (Nov. 1934), 5 , p. 190.

40. Datar, N.S., Iyengar, R.K., P. Sridhar, Rao, M.R.V.; Proceedings of International Symposium on Modern Developments in Steel making, Jamshedpur, India , (1981), p. 203-223.